Supporting information

A Carbon-Carbon Bond Formation on Bis(oxazolinyl)phenyl-Rhodium Complex in Reduction and Oxidative Addition Sequence

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General Procedures. ^{1}H and ^{13}C NMR spectra were obtained at 25 ˚C on a Varian Mercury 300 spectrometer. ^{1}H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for chloroform. ^{13}C NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.0 ppm for $CDCl_3$ as an internal standard. Infrared spectra were recorded on a JASCO FT/IR-230 spectrometer.

Preparation of (*t*Bu-Phebox-*dm*)H. A suspension of 5-*tert*-butylisophthalic acid (1.11 g, 5.0 mmol) in thionyl chloride (7.0 ml) was refluxed for 5 h and then excess thionyl chloride was removed under reduced pressure to give 5-*tert*-butylisophthaloyl chloride, which was used in next step without further purification.

To a solution of 2-amino-2-methylpropan-1-ol (0.89 g, 10 mmol) and triethylamine (12 mL) in dichloromethane (40 mL) was added 5-*tert*-butylisophthaloyl chloride at 0 °C. The mixture was stirred at room temperature for 1 h. Methanesulfonyl chloride (1.5 ml, 20 mmol) was added at 0 °C, and then the mixture was stirred at room temperature for 16 h. At 0 °C, aqueous potassium carbonate (1M, ca 10 mL) was added and the mixture was extracted with ethyl acetate (20 mL x 3). The organic layer was washed with saturated brine, was dried over sodium sulfate, and was concentrated. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane 1:3) to give (*t*Bu-Phebox-*dm*)H in 82 % (1.34 g, 4.09 mmol) as colorless solid; mp: 166 °C. ^{1}H NMR (300 MHz, $CDCl_3$):δ1.35 (s, 9H), 1.36 (s, 12H), 4.07 (s, 4H), 8.03 (d, J_{HH} = 1.5 Hz, 2H), 8.31 (t, J_{HH} = 1.5 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ28.46, 31.29, 34.99, 67.73, 79.00, 125.6, 127.7, 128.0, 151.4, 161.5 ppm. IR (KBr, cm^{-1}): ν 1650, 1358. Anal Calcd for $C_{20}H_{28}N_2O_2$·0.5(H_2O): C, 71.19; H, 8.66; N, 8.30; Found: C, 71.36; H, 8.73; N, 8.25.

Preparation of (*t*Bu-Phebox-*dm*)$RhCl_2(H_2O)$ (1): To $RhCl_3$·$3H_2O$ (579 mg, 2.2 mmol), (*t*Bu-Phebox-*dm*)H (657 mg, 2.0 mmol) and sodium bicarbonate (168 mg, 2.0 mmol) were added methanol (20 mL) and H_2O (1 mL). The mixture was stirred at 60 °C

for 18 h. After removal of the solvent, the residue was extracted with ethyl acetate and the extract was filtrated through celite. The concentrated residue was purified by silica gel column chromatography with ethyl acetate/hexane (1:1) to give **1** in 62 % yield (641 mg, 1.23 mmol) as air-stable brownish solids; mp: 313 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 9H), 1.56 (s, 12H), 3.70 (s, 2H), 4.53 (s, 4H), 7.66 (s, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 27.73, 31.71, 34.99, 66.13, 82.35, 125.6, 130.9, 146.9, 169.0, 174.1 (d, J_{RhC} = 25.1 Hz). IR (KBr cm^{-1}): 1626, 1446. Anal calcd for $C_{20}H_{29}Cl_2N_2O_3Rh \cdot 0.5(CH_2Cl_2)$: C, 43.83; H, 5.38; N, 4.98; Found: C, 43.98; H, 5.36; N, 4.76.

Preparation of 2. A mixture of **1** (52 mg, 0.10 mmol), diisopropylamine (140 μL, 1.0 mmol) and molecular sieves 4Å (60 mg) in dichloromethane (2.0 mL) was stirred at 50 ^{o}C for 12 h under an argon atmosphere. After filtration of insoluble materials, the solvent was removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/hexane at room temperature to give **2** (29 mg, 0.050 mmol, 50%) as air-stable yellow crystals; mp: 210 ^{o}C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 0.79 (td, J_{HH} = 7.2, J_{RhH} = 2.1 Hz, 2H), 1.25 (s, 6H), 1.32 (s, 9H), 1.57 (s, 6H), 1.61 (d, J_{HH} = 6.9 Hz, 6H), 2.16 (s, 3H), 2.57 (t, J_{HH} = 7.2 Hz, 2H), 4.27 (d, J_{HH} = 8.4 Hz, 2H), 4.47 (d, J_{HH} = 8.4 Hz, 2H), 5.85 (sep, J_{HH} = 6.9 Hz, 1H), 7.49 (s, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, rt): δ 11.23 (d, J_{RhC} = 23.5 Hz), 21.41, 22.52, 26.96, 28.36, 31.74, 34.75, 49.43, 52.22, 66.09, 82.09, 123.4, 130.1, 143.6, 170.7 (d, J_{RhC} = 5.1 Hz), 182.3 (d, J_{RhC} = 1.7 Hz), 187.4 (d, J_{RhC} = 24.1 Hz). IR (KBr cm^{-1}): 1650, 1364. Anal calcd for $C_{27}H_{41}ClN_3O_2Rh \cdot 0.5(C_4H_8O_2)$: C, 56.00; H, 7.29; N, 6.76; Found: C, 56.05; H, 7.35; N, 6.82.

Preparation of 2-d_2. A mixture of **1** (10 mg, 0.019 mml), diisopropylamine (108 μL, 0.77 mmol) and molecular sieves 4A (100 mg) in dichloromethane-d_2 (0.6 mL) was stirred at 50 ^{o}C for 8 h under an argon atmosphere. After filtration, the solvent was removed under reduced pressure. The residue was passed through column chromatography on silica gel (ethyl acetate) and the eluent was recrystallized from CH_2Cl_2/hexane at room temperature to give **2-d_2** (5.4 mg, 0.0093 mmol, 48%) as yellow crystals.

Preparation of 3. A mixture of **1** (52 mg, 0.10 mmol) and isopropylamine (340 μL, 4.0 mmol) in CH_2Cl_2 (1.5 mL) was stirred at 45 ^{o}C for 12 h under an argon atmosphere. After removal of the solvent, the residue was extracted with ethyl acetate and the extract

was filtrated. The filtrate was purified by column chromatography on silica gel (ethyl acetate/MeOH = 10:1) to give **3** (28.1 mg, 0.050 mmol, 50 %) as brown solids; mp: 215 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.59 (d, J_{HH} = 6.3 Hz, 6H), 1.38 (s, 9H), 1.64 (s, 6H), 1.77 (s, 6H), 1.96 (sep, J_{HH} = 6.3 Hz, 1H), 2.70 (brs, 2H), 4.52 (d, J_{HH} = 8.1 Hz, 2H), 4.59 (d, J_{HH} = 8.1 Hz, 2H), 7.69 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 24.02, 27.63, 28.55, 31.72, 35.10, 45.60, 66.59, 82.94, 125.5, 130.9, 146.8, 171.3, 185.6 (d, J_{RhC} = 22.3 Hz). IR (KBr cm^{-1}): 3448, 3239, 1627, 1452. Anal calcd for $C_{23}H_{36}Cl_2N_3O_2Rh\cdot(H_2O)$: C, 47.76; H, 6.62; N, 7.27; Found: C, 47.42; H, 6.55; N, 6.97.

Preparation of 5. A mixture of **1** (104 mg, 0.20 mmol), triethylamine (0.56 mL, 4.0 mmol) and molecular sieves 4A (0.5g) in dichloromethane (3.0 mL) was stirred at 50 ^{o}C for 12 h under an argon atmosphere. After removal of the solvent, the residue was extracted with ethyl acetate and the extract was filtrated. The filtrate was purified by column chromatography on silica gel (ethyl acetate) to give **5** (75 mg, 0.12 mmol, 60 %) as yellow solids. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, J_{HH} = 7.2 Hz, 9H), 1.34 (s, 9H), 1.61 (s, 6H), 1.78 (s, 6H), 2.93 (q, J_{HH} = 7.2 Hz, 6H), 3.41 (d, J_{RhH} = 3.3 Hz, 2H), 4.34 (d, J_{HH} = 8.1 Hz, 2H), 4.49 (d, J_{HH} = 8.1 Hz, 2H), 7.56 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 8.22, 28.27, 29.01, 31.70, 34.87, 48.79 (d, J_{RhC} = 34.7 Hz), 54.21, 67.74, 82.44, 124.6, 130.8, 144.8, 170.4, 189.5 (d, J_{RhC} = 24.0 Hz). IR (KBr cm^{-1}): 1620, 1450.

Preparation of 6. A mixture of **1** (52 mg, 0.10 mml), methyl chloroacetate (44 μl, 0.50 mmol) and molecular sieves 4A in dichloroethane (2 mL) was stirred at 50 ^{o}C for 6 h under an argon atmosphere. After removal of the solvent, the residue was purified by column chromatography on silica gel (ethyl acetate then acetone) to give **6** (52.7 mg, 0.095 mmol, 95 %) as yellow solids; mp: 218 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (s, 9H), 1.58 (s, 6H), 1.62 (s, 6H), 2.20 (brs, 2H), 2.38 (d, J_{RhH} = 3.6 Hz, 2H), 2.76 (s, 3H), 4.50 (s, 4H), 7.53 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 4.12 (d, J_{RhC} = 27.5 Hz) 27.08, 28.60, 31.64, 34.95, 50.01, 66.25, 82.51, 123.8, 130.9, 145.4, 170.5, 179.2, 184.2 (d, J_{RhC} = 25.7 Hz). IR (KBr, cm^{-1}): 1696, 1442. Anal calcd for $C_{23}H_{24}ClN_2O_5Rh\cdot0.5(C_4H_8O_2)$: C, 49.97; H, 6.37; N, 4.66; Found: C, 49.78; H, 6.47; N, 4.61.

Reaction of 5 with *N*–isopropylpropylideneamine. A mixture of 4 (20 mg, 0.032 mmol), *N*-isopropylpropylideneamine (22 μL, 0.16 mmol) and molecular sieves 4A (0.5 g) in THF (1 mL) was stirred at 50 ^{o}C for 20 h under an argon atmosphere. The mixture was filtrated and the filtrate was evaporated. The residue was extracted with ethyl

acetate and the extract was filtrated again. The filtrate was purified by column chromatography on silica gel to give a mixture of **2** and **3** (8.1 mg) and **1** (5.9 mg, 0.011 mmol, 34 %). The yields of **2** and **3** were determined to be 28 and 17 %, respectively, on the basis of the ^{1}H NMR spectrum.

X-ray analysis. Single crystals of **2** and **6** suitable for X-ray diffraction study were obtained from hexane/ethyl acetate/dichloromethane solution and hexane/ethyl acetate at room temperature, respectively. The diffraction data were collected on a Brucker SMART APEX CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). An empirical absorption correction was applied by using SADABS. The structure was solved by direct method and refined by full-matrix lease-square on F^2 using SHELXTL. All non-hydrogen atoms except the disordered ^{t}Bu group of **2** were refined with anisotropic displacement parameters. Hydrogen atoms on O(5) of **6** were located on a difference Fourier map and refined with a isotropic thermal parameter.