Supplementary Material for

Trifluoromethyl-Substituted Indenyl Rhodium and Iridium Complexes Are Highly Selective Catalysts for Directed Hydroboration Reactions

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Experimental Section

General Experimental Conditions. Proton magnetic resonance (^{1}H NMR) spectra were recorded on Bruker ARX300 and Bruker DPX300 spectrometers using tetramethylsilane (TMS) as internal reference. Chemical shifts are reported on the δ scale in parts per million (ppm) downfield from TMS; peak multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet), and br (broad); coupling constants (*J*) are reported in Hertz. Carbon magnetic resonance (^{13}C NMR) spectra were recorded on Bruker ARX 300 and Bruker DPX 300 spectrometers using the carbon signal of the deuterated solvent as the internal reference. Infrared spectra (IR) were recorded on a Midac FTIR spectrometer. Peaks are reported in cm^{-1}. Elemental analysis were performed by Robertson Microlit Laboratories, Inc., Madison, NJ.

Analytical thin layer chromatography (TLC) was performed on Macherey-Nagel Polygram® Sil G/UV$_{254}$ silica gel plates with 0.2 mm thick, 254-F indicator; visualization was accomplished by UV (254 nm) illumination and by staining with potassium permanganate ($KMnO_4$) in an aqueous solution of potassium carbonate. Flash chromatography was performed according to Still[i] with use of silica gel (0.040-0.063 mm, E. Merck). High pressure liquid chromatography (HPLC) was performed with a Waters Nova-Pak C-18 column (Waters Instrument Co., 3.9 x 150 mm) on a Waters liquid chromatogram with a UV detector.

All reactions were performed under a dry nitrogen or dry argon atmosphere in oven dried (120 °C) or flame dried glassware. Reaction mixtures were stirred magnetically unless otherwise indicated. Air sensitive liquids and solutions were transferred *via* syringe or cannula and introduced into reaction vessels through rubber septa. Tetrahydrofuran (THF) was distilled from sodium and benzophenone under an argon atmosphere. Hexane was distilled from calcium hydride under an argon atmosphere. Brine refers to a saturated aqueous solution of sodium chloride.

The (±)- 4-benzyloxycyclohexene substrate for the catalytic reaction was prepared from (±)-3-cyclohexen-1-ol.[ii] Authentic standards for product analysis, cis and trans-3-benzyloxycyclohexanol, cis and trans-4-benzyloxycyclohexanol were prepared as previously reported.[iii] Catecholborane was prepared as previously reported[iv] and purified by vacuum distillation (bp 36-38 °C (50 mm), [lit.[iv] bp 76-77 °C (100 mm)].

Preparation of Catalysts. The trifluoromethyl-substituted indenes (1-trifluoromethylindene (**3**), 2-trifluoromethylindene (**4**), 1,3-bistrifluoromethylindene (**5**)) were prepared using previously reported procedures.[v] The following organometallic complexes and catalysts were prepared using previously reported procedures: di-µ-chlorobis(1,5-cyclooctadiene)dirhodium (I),[vi] di-µ-chloro-tetrakis(ethylene)dirhodium (I),[vi] di-µ-chlorobis(1,5-cyclooctadiene)diiridium (I),[vii] bis(ethylene)indenylrhodium,[viii] indenyl(1,5-cyclooctadiene)rhodium,[viii] indenyl(1,5-cyclooctadiene)iridium,[ix] 1-trifluoromethylindenyl(1,5-cyclooctadiene)rhodium,[x] 1-trifluoromethylindenyl(1,5-cyclooctadiene)iridium,[x] 1,3-bis(trifluoromethyl)indenyl(1,5-cyclooctadiene)rhodium.[x]

2-Trifluoromethylindenyl(1,5-cyclooctadiene)rhodium. A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with potassium hydride (0.06 g, 1.40 mmol) and 30 mL of anhydrous THF under a dry argon atmosphere. The reaction mixture was cooled to -30 °C and 2-trifluoromethylindene (0.36 g, 2.0 mmol) was added *via* syringe. The mixture was stirred at -30 °C for

30 min and di-µ-chlorobis(1,5-cyclooctadiene)dirhodium (I) (0.20 g, 0.40 mmol) was added. After stirring for 30 min at -30 °C the solvent was removed under reduced pressure. The residue was triturated with 15 mL of hexane and filtered through a layer of celite. Removal of the hexane under reduced pressure provided 0.128 g (40%) of (2-CF_3Ind)Rh(COD) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 7.17-7.11 (m, 2H), 5.42 (s, 2H), 4.13 (s, 4H), 1.94-1.72 (m, 8H).

Anal. Calcd for $C_{18}H_{18}F_3Rh$: C, 54.84; H, 4.60. Found: C, 54.54; H, 4.53.

2-Trifluoromethylindenyl(1,5-cyclooctadiene)iridium. A 200 mL Schlenk flask equipped with a magnetic stir bar was charged with potassium hydride (0.09 g, 2.20 mmol) and 75 mL of anhydrous THF under a dry argon atmosphere. The reaction mixture was cooled to -30 °C and 2-trifluoromethylindene (0.32 g, 1.76 mmol) was added *via* syringe. The mixture was stirred at -30 °C for 30 min and di-µ-chlorobis(1,5-cyclooctadiene)diiridium (I) (0.30 g, 0.44 mmol) was added. After stirring for 30 min at -30 °C and 30 min at room temperature the solvent was removed under reduced pressure. The residue was triturated with 50 mL of hexane. The solvent portion was transferred to a flash column packed with neutral alumina and eluted with hexane to provide 0.28 g (66%) of (2-CF_3Ind)IrCOD as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.16 (m, 4H), 5.56 (s, 2H), 4.08 (s, 4H), 1.80-1.56 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.6 (q, J_{CF} = 268 Hz), 124.9, 120.7, 110.4, 92.9 (q, J_{CCF} = 38 Hz) 68.1, 53.2, 32.7.

Anal. Calcd for $C_{18}H_{18}F_3Ir$: C, 44.71; H, 3.75. Found: C, 44.65; H, 3.88.

1,3-bis(trifluoromethyl)indenyl(1,5-cyclooctadiene)iridium. A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with potassium hydride (0.04 g, 0.89 mmol) and 30 mL of anhydrous THF under a dry argon atmosphere. The reaction mixture was cooled to -30 °C and 1,3-bis(trifluoromethyl)indene (0.19 g, 0.75 mmol) was added *via* syringe. The mixture was stirred at -30 °C for 30 min and di-µ-chlorobis(1,5-cyclooctadiene)diiridium (I) (0.20 g, 0.30 mmol) was added. After stirring for 60 min at -30 °C the solvent was removed under reduced pressure. The residue was triturated with 15 mL of hexane and filtered through a layer of celite. Removal of the hexane provided 0.9 g (28%) of a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.40-7.36 (m, 2H), 6.63 (s, 1H), 4.12 (s, 4H), 1.83-1.68 (m, 8H).

Anal. Calcd for $C_{19}H_{17}F_6Ir$: C, 41.38; H, 3.11. Found: C, 41.31; H, 2.93.

General Catalytic Procedure. Under an atmosphere or argon, a solution of 4-(benzyloxy)cyclohexene (100 mg, 0.53 mmol) in anhydrous hexane (1 mL) was added by syringe to a solution of IndRh(Cod) (17 mg, 0.053 mmol) in anhydrous hexane (4 mL). The light yellow solution was cooled in an ice bath and catecholborane (0.150 mL, 1.38 mmol) was added to give a pale yellow solution. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was then cooled in an ice bath and MeOH (2 mL), NaOH (3 N, 2 mL), and 30% H_2O_2 (2 mL) was added. The mixture was stirred, with slow warming to room temperature, for 1 h. The reaction mixture was extracted with ether, dried over $MgSO_4$ (anhyd) and concentrated. The selectivity was determined by HPLC analysis with a reverse phase column (Waters Nova-Pak C-18, 3.9 x 150 mm) using a solvent gradient of 10% acetonitrile / water to 100% acetonitrile over a 20 min period. The isomers eluted in the following order: trans-1,4 (13.1 min), cis-1,3 (13.4 min), cis-1,4 (13.6 min), trans-1,3 (13.8 min).

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