Supplementary Information

Regioselective Functionalization of Alkanes by Sequential Dehydrogenation-Hydrozirconation

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Materials and methods. All reactions were carried out using dried test tubes under argon atmosphere. Dodecane (**1**), butylbenzene (**5**), 1,2-dichloroethane, and tetrahydrofuran (THF) were dried and degassed via freeze-pump-thaw cycles. The iridium complex, $IrH_5(P^iPr_3)_2$, was prepared according to the literature method.[1] All other reagents were purchased and used without further purification.

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to Me_4Si (TMS) at δ 0.00 ppm or residual solvent peak ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm.

All product compounds are known. The structures of the reaction products were determined by comparing the spectral data of the products to the spectral data of 1-bromododecane (**4a**),[2] 1-iodododecane (**4b**),[3] 1-dodecanol (**4c**),[4] 1-pentadecene (**4d**),[5] 1-tridecanal (**4e**),[6] and 1-iodo-4-phenylbutane (**6**).[7]

Investigation of sequential dehydrogenation-hydrozirconation using an iridium-pincer complex. At first, an iridium-pincer complex (Figure S1) was selected because it is a known catalyst for transfer dehydrogenation-hydrogenation reactions of alkanes.[8] Unfortunately, in many cases using this and other iridium-pincer complexes, cyclooctane was used as a substrate and only a few examples of dehydrogenation of linear alkanes have been reported.[9] Using the iridium-pincer complex, we carried out dehydrogenation of alkanes and successive hydrozirconation. However, the iridium-pincer complex did not give the desired result because the iridium-pincer complex and the presence of base inhibited the hydrozirconation process.

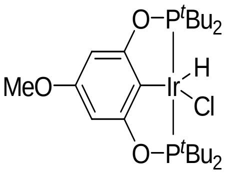

Figure S1. Structure of the iridium-pincer complex.

Synthesis of 4b (**Table 1, entry 1).** After hydrozirconation, I_2 (**3b**, 12.7 mg, 50 μmol) was added and the reaction mixture was stirred at 25 °C for 1 h. The resulting solution was concentrated and filtered through a silica gel pad (hexane). After distillation, **4b** was obtained as a colourless oil (11.0 mg, 74%).

Synthesis of 4c (Table 1, entry 2). After hydrozirconation, 1,2-dichloroethane (1.25 mL) and 5.5 M solution of *t*-BuOOH in decane (**3c**, 9.1 μL, 50 μmol) were added to the reaction mixture at 0 °C and the mixture was stirred for 4 h. The resulting solution was treated with water, the organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. After purification by column chromatography (hexane, then diethyl ether), **4c** was obtained as a colourless oil (5.4 mg, 58%).

Synthesis of 4d (Table 1, entry 3). After hydrozirconation, allyl bromide (**3d**, 4.3 μL, 50 μmol) and CuCl (1.0 mg, 10 μmol) were added and the reaction mixture was stirred at 40 °C for 1 h. The resulting solution was concentrated in vacuo and filtered through a silica gel pad (hexane). The yield of **4d** was determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard (57%).

Synthesis of 4e (Table 1, entry 4). After hydrozirconation, the mixture was stirred at 25 °C for 3 h under CO (**3e**) atmosphere. After the resulting solution was treated with 1.0 M HCl (50.0 μL, 50.0 μmol), the mixture was stirred at 25 °C for 2 h. The resulting mixture was treated with water, and the organic layer was separated and the aqueous layer was extracted with hexane. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography (hexane, then hexane/ethyl acetate = 20:1) gave **4e** as a colourless oil (4.5 mg, 44%).

Procedure for dehydrogenation of 5 (eqn (2)). A mixture of $IrH_5(P^iPr_3)_2$ (28 mg, 55 μmol), 3,3-dimethyl-1-butene (128 μL, 0.99 mmol), and **1** (3.4 mL, 22 mmol) was stirred at 150 °C for 12 h under an argon atmosphere. After the reaction mixture was cooled to 25 °C, 3,3-dimethyl-1-butene and 2,2-dimethylbutane, which was derived by hydrogenation of 3,3-dimethyl-1-butene, were removed in vacuo. The ^{1}H NMR spectrum indicated the formation of a mixture of internal alkenes. Under the reaction conditions, 4-phenyl-2-butene and 4-phenyl-1-butene were not observed in ^{1}H NMR spectrum.

Procedure for hydrozirconation of alkenes (eqn (2)). After dehydrogenation of alkane, THF (17.2 mL), and Cp_2ZrHCl (**2**, 38.7 mg, 0.15 mmol) were added to the reaction mixture under argon atmosphere. After stirring at 40 °C for 24 h, the mixture was cooled to 25 °C.

Synthesis of 6 (eqn (2)). After dehydrogenation of butylbenzene (**5**) and hydrozirconation, **3b** (12.7 mg, 50 μmol) was added and the reaction mixture was stirred at 25 °C for 1 h. The resulting solution was concentrated in vacuo and filtered through a silica gel pad (hexane). To clarify ^{1}H NMR spectrum, almost all of **5** was removed by high vacuum pump (0.22 torr, 25 °C). The yield of **6** was determined by ^{1}H NMR analysis of the resulting solution with 1,1,2,2-tetrachloroethane as an internal standard (30%).

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