

Supporting Information

**Dehydrocoupling of Dimethylamine-Borane Catalysed by Rhenium
Complexes and its Application in Olefin Transfer-Hydrogenations**

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Experimental Details

General Experimental.

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N₂ by employing standard procedures and were degassed by freeze-thaw cycles prior to use. [Re(NO)(η^2 -H₂)(Br)₂(PⁱPr₃)₂] (**1a**), [Re(NO)(η^2 -H₂)(Br)₂(PCy₃)₂] (**1b**), [Re(NO)(PⁱPr₃)₂(CH₃CN)(Br)₂] (**2a**), [Re(NO)(PCy₃)₂(CH₃CN)(Br)₂] (**2b**) were prepared according to reported procedures.¹ Me₂NH·BH₃ was purchased from Fluka and used without further purification..

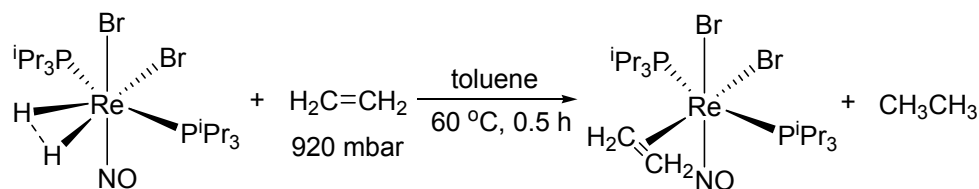
Analysis.

¹H NMR, ¹³C{¹H} NMR, ³¹P{¹H} NMR and ¹¹B{¹H} NMR data were recorded on a Varian Gemini-300 spectrometer. Chemical shifts are expressed in parts per million (ppm) referenced to the deuterated solvent used. All chemical shifts for the ³¹P{¹H} NMR data are reported downfield in ppm relative to external 85% H₃PO₄ at 0.0 ppm. All chemical shifts for the ¹¹B{¹H} NMR data are reported in ppm relative to external BF₃ in diethyl ether at 0.0 ppm. Signal patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were obtained by using ATR methods with a Bio-Rad FTS-45 FTIR spectrometer.

Synthesis of [Re(NO)(PⁱPr₃)₂(η^2 -C₂H₄)(Br)₂] (3a**)**

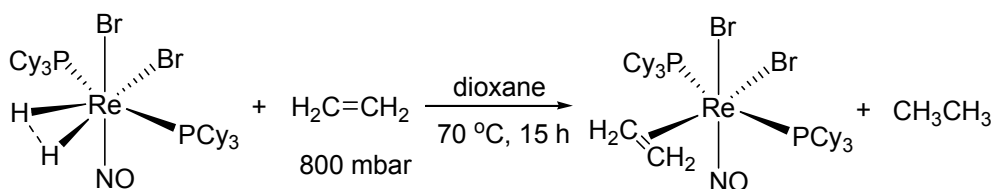
In Young-Schlenk flask, 150 mg of rhenium complex **1a** (0.21 mmol) and 5 mL dioxane were added. After freezing the solution, the N₂ atmosphere was exchanged with 920 mbar of ethylene gas. The mixture was stirred at 60 °C for 30 min and pink precipitate formed. After stirring at rt for another 10 h, pink precipitate **3a** was separated (146 mg, 92%). ¹H-NMR (300.1 MHz, toluene-d₈, ppm): δ 1.17-1.24 (m, 18H, CH₃), 1.26-1.33 (m, 18H, CH₃), 2.37 (td, 2H, ²J = 3 Hz, ³J = 12 Hz, CH₂=), 2.94 (td, 2H, ²J = 3 Hz, ³J = 12 Hz, CH₂=), 3.06 (m, 6H, CH). ¹³C{¹H} NMR (75.5

MHz, toluene- d_8 , ppm) : δ 19.6 (s, CH₃), 19.9 (s, CH₃), 26.2 (t, J (PC) = 10.6 Hz, CH), 39.5 (br, CH₂=CH₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, toluene- d_8 , ppm): δ -12.3 (s); IR (ATR): ν (NO): 1693 cm^{-1} ; Anal. Calcd. for C₂₀H₄₆Br₂NOP₂Re: C, 33.19; H, 6.41 ; N, 1.94. Found: C,33.39; H, 6.52; N, 1.93.



Synthesis of [Re(NO)(PCy₃)₂(η^2 -C₂H₄)(Br)₂] (**3b**)

In Young-Schlenk flask, 450 mg of rhenium complex **1b** (0.47 mmol) and 10 mL dioxane were added. After freezing the solution, the N₂ atmosphere was exchanged with 800 mbar of ethylene gas. The mixture was stirred at 70 °C for 15 h and brown-pink precipitate was collected (420 mg, 89%).²



Catalytic Dehydrocoupling of Me₂NH·BH₃ by Rhenium Complexes

Catalytic Dehydrocoupling of Me₂NH·BH₃. To a solution of Me₂NH·BH₃ (59 mg, 1.0 mmol) in dioxane (0.5 mL), a catalytic amount of the appropriate complex (0.01 mmol) was added and the solution was heated at 85 °C. After 4 h, the reaction mixture was analyzed by ¹¹B-NMR to determine the conversion of Me₂NH·BH₃ into *N,N*-dimethylcycloborazane.

Catalytic Transfer-hydrogenation of Olefins by Rhenium Complexes

Catalytic transfer-hydrogenation of alkenes. To a solution of Me₂NH·BH₃ (59 mg, 1.0 mmol) and the olefin (1.0 mmol) in dioxane (0.5 mL), a catalytic amount of the appropriate complex (0.01 mmol) was added and the solution was stirred vigorously at 85 °C. After appropriate reaction time the product formation was analyzed by ¹¹B{¹H} NMR, ¹H NMR and ¹³C{¹H} NMR spectroscopy.

References

1. D. Gusev, A. Llamazares, G. Artus, H. Jacobsen, H. Berke, *Organometallics*, 1999, **18**, 75; A. Choualeb, O. Blacque, H. W. Schmalle, H. Berke, *Dalton Trans*, submitted.
2. A. Choualeb, E. Maccaroni, H. W. Schmalle, H. Berke, *Dalton Trans*, to be submitted