Supporting Information for "Lewis Acid-Promoted Molybdenum Nitride-Alkyne Metathesis"

General

Materials. Unless otherwise stated, all starting materials and reagents were purchased from commercial sources and used without further purification. $MoN(OTMS)_2[N(TMS)_2]$ (**2**)[i] and $MoN(O\textit{t}\text{-}Bu)_3$ (**3**)[ii] were prepared according to literature procedures. $B(C_6F_5)_3$ was purified by sublimation. All solvents were purified according to the method of Grubbs.[iii]

General Methods. All reactions were prepared in an argon-filled glove box and run under an inert atmosphere. The reaction vessels used, unless otherwise specified, were 5 mL vials fitted with PTFE/silicone septa. All glassware was oven-dried before use. Reactions were monitored by gas chromatography using dodecane as an internal standard.

Physical Characterization. ^1H spectra were referenced to residual solvent peaks or TMS (δ = 0 ppm). ^{19}F NMR was calibrated using $CFCl_3$ (δ = 0 ppm) as an external standard. ^{11}B NMR was calibrated using $BF_3{\cdot}Et_2O$ (δ = 0 ppm) as an external standard. Chemical shifts (δ) are expressed in parts per million (ppm). Splitting constants (J) are expressed in Hz. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; dd, doublet of doublets; td, triplet of doublets; m, multiplet. ATR-IR was performed on isolated substrates without solvent. Gas chromatography samples were injected onto a capillary column. The injector temperature was 250 °C and the detector temperature was 280 °C with a H_2 carrier gas flow of 16 mL/min. The column temperature program was as follows: 100 °C for 3 min, ramp to 300 °C at 40 °C/min, then hold for 3 min for a total run time of 11.00 min.

Synthetic Procedures

$MoN(OTMS)_2[N(TMS)_2] \cdot B(C_6F_5)_3$ (2-B). In a glove box, **2** (50 mg, 0.111 mmol) was dissolved in dichloromethane (1 mL). $B(C_6F_5)$ (57 mg, 0.111 mmol) was added, causing the pale yellow solution to darken slightly. Colorless crystals suitable for X-ray analysis were grown by slow diffusion of pentane into the solution at -30 °C under argon.
NMR (CD_2Cl_2, 400 MHz): ^{1}H: δ 0.317 (s, 18H); 0.141 (s, 18H). ^{19}F: δ -131.4 (d, J = 18.8 Hz, 6F); -159.8 (t, J = 18.8 Hz, 3F); -165.58 (td, J = 18.8 Hz, 7 Hz, 6F). ^{11}B: -3.43 ($LW_{1/2}$ = 135 Hz).

$MoN(O\textit{t}\text{-}Bu)_3 \cdot B(C_6F_5)_3$ (3-B). In a glove box, **3** (30 mg, 0.091 mmol) was dissolved in dichloromethane (1 mL). $B(C_6F_5)$ (45 mg, 0.091 mmol) was added, causing the colorless solution to turn yellow. Colorless crystals suitable for X-ray analysis were grown by slow diffusion of pentane into the solution at -30 °C under argon; these crystals decomposed quickly when taken out of solution. Crystallographic analysis indicated that crystals of **3-B** contained one highly disordered pentane per asymmetric unit which could not be suitably refined; prior to final refinement, the pentane was removed using PLATON/SQUEEZE.[iv]
NMR (CD_2Cl_2, 400 MHz): ^{1}H: δ 1.313 (s). ^{19}F: -132.0 (dd, J = 24 Hz, 8 Hz); -159.3 (t, J = 24 Hz); -165.6 (td, J = 24 Hz, 8 Hz). δ. ^{11}B: -4.28 ($LW_{1/2}$ = 114 Hz). IR (ATR, cm^{-1}): 2986, 1644, 1516, 1457, 1394, 1367, 1282, 1244, 1155, 1058, 974, 935, 914, 858, 790, 770, 738, 678. Anal. Calc'd for $C_{30}H_{27}BF_{15}MoNO_3$: C 42.83, H 3.23; N 1.66; Found: C 42.54, H 3.26, N 1.70.

Typical procedure for alkyne metathesis screens in Table 1, Entries 1, 3, and 5. In a glove box, **2** (10 mg, 0.022 mmol) was dissolved in toluene (1 mL). $B(C_6F_5)_3$ (22 mg, 0.044 mmol) was added and the solution stirred until the $B(C_6F_5)_3$ dissolved. 2-trifluoromethylphenol (11 mg, 0.066 mmol) was added, resulting in a distinct color change from yellow to deep red. Dodecane (20 μL) and alkyne(s) (0.22 mmol) were added, the vial sealed, and heated to 90 °C. For Entry 3, 0.22 mmol each of

diphenylacetylene and 3-hexyne were added. 20 μL aliquots of the reaction mixture were diluted to 1 mL with EtOAc and analyzed by gas chromatography.

Typical procedure for alkyne metathesis screens in Table 1, Entries 2, 4, and 6. Same as above, but with no $B(C_6F_5)_3$ added.

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[i] M. Bindl, R. Stade, E. K. Heilmann, A. Picot, R. Goddard and A. Fürstner, *J. Am. Chem. Soc.*, 2009, **131**, 9468-9470.
[ii] D. M.-T. Chan, M. H. Chisholm, K. Felting, J. C. Huffman and N. S. Marchant, *Inorg. Chem.*, 1986, **25**, 4170–4174.
[iii] Pangborn, A. B., Giardello, M. A., Grubbs, R. H., Rosen, R. K., and Timmers, F. J. *Organometallics* 1996, **15**, 1518-1520.
[iv] Spek, A. L. and van der Sluis, P. *Acta Cryst.* 1990, **A46**, 194-201.