

## Supporting Information for

### Synthesis of Molybdenum Nitrido Complexes for Triple-Bond Metathesis of Alkynes and Nitriles

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## ACM Studies

General Procedure: [Mo] (5.0 mg) and an internal standard of 1,3,5-trimethoxybenzene were dissolved in C<sub>6</sub>D<sub>6</sub> (0.50 mL) to give a catalyst concentration of 10 mg mL<sup>-1</sup>. The solution was transferred to a J. Young tube and 1-phenyl-1-butyne (20 equiv) was added *via* syringe. The sample was frozen and the overlying atmosphere was removed *in vacuo*. The J. Young tube was heated at the desired temperature and the reaction was monitored by <sup>1</sup>H NMR spectroscopy.

**NMo(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>(NHMe<sub>2</sub>) (12).** Following the general procedure at 75 °C: **12** (5.0 mg, 0.0073 mmol), 1-phenyl-1-butyne (20.0 μL, 0.141 mmol). After 2.5 hours, a 25 % conversion to diphenylacetylene was observed.

**NMo(OSiPh<sub>3</sub>)<sub>3</sub>(NHMe<sub>2</sub>) (5-NHMe<sub>2</sub>):** Following the general procedure at 75 °C: **5-NHMe<sub>2</sub>** (5.0 mg, 0.0051 mmol), 1-phenyl-1-butyne (14.5 μL, 0.102 mmol). After 1.5 hours, a 25 % conversion to diphenylacetylene was observed.

**NMo(OSiPh<sub>3</sub>)<sub>3</sub> (5).** Complex **5** (6.7 mg, 0.0072 mmol, 1.0 equiv) and an internal standard of 1,3,5-trimethoxybenzene were dissolved in C<sub>6</sub>D<sub>6</sub> (0.7 mL), then the solution was transferred to a J. Young tube. Neat 1-phenyl-1-butyne (5.1 μL, 0.036 mmol, 5.0 equiv) was added and the reaction was monitored by <sup>1</sup>H NMR spectroscopy at room temperature. After 5 hours, a 25 % conversion to diphenylacetylene was observed.

**NMo(OSiPh<sub>2</sub><sup>t</sup>Bu)<sub>3</sub> (16).** Following the general procedure at 90 °C: **16** (20.0 μL of a 0.25 mg μL<sup>-1</sup> stock solution in C<sub>6</sub>D<sub>6</sub>, 0.0057 mmol), 1-phenyl-1-butyne (16.0 μL, 0.113 mmol). After 9 hours, no metathesis products were observed.

**NMo(OCPh<sub>2</sub>Me)<sub>3</sub> (17).** Following the general procedure at 75 °C: **17** (5.1 mg, 0.0074 mmol), 1-phenyl-1-butyne (21.0 μL, 0.148 mmol). After 21 hours, no metathesis products were observed and **17** had completely decomposed

### NACM Concentration Studies With **5**

General Procedure: Complex **5**, anisonitrile (10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were dissolved in bromobenzene-*d*<sub>5</sub> at the desired concentration of **5**, then the solution was transferred to a J. Young tube. Then 1-phenyl-1-butyne (10 equiv) was introduced *via* syringe and the overlying atmosphere was removed *in vacuo*. The reaction was heated at 180-185 °C and monitored by <sup>1</sup>H NMR spectroscopy. The results are reported in Table S1.

20 mg mL<sup>-1</sup> Following the general procedure: **5** (10.0 mg, 0.011 mmol), anisonitrile (14.6 mg, 0.11 mmol), 1-phenyl-1-butyne (15.2 μL, 0.11 mmol), bromobenzene-*d*<sub>5</sub> (5.0 mL).

30 mg mL<sup>-1</sup> Following the general procedure: **5** (15.0 mg, 0.016 mmol), anisonitrile (21.3 mg, 0.16 mmol), 1-phenyl-1-butyne (23.0 μL, 0.16 mmol), bromobenzene-*d*<sub>5</sub> (5.0 mL).

40 mg mL<sup>-1</sup> Following the general procedure: **5** (20.0 mg, 0.021 mmol), anisonitrile (28.0 mg, 0.21 mmol), 1-phenyl-1-butyne (30.4  $\mu$ L, 0.21 mmol), bromobenzene-*d*<sub>5</sub> (5.0 mL).

**Table S1.** NACM studies with **5**.

Concentration (mg mL <sup>-1</sup> )	Time (h)	ArCCPh <sup>a</sup> (%) <sup>b</sup>	+/-	ArCCEt <sup>a</sup> (%) <sup>b</sup>	+/-	Total (%)	+/-
20	4	5.33	0.62	3.67	0.85	9.00	1.47
	8	7.33	0.62	5.33	0.62	12.66	1.24
	12	8.50	0.00	5.50	0.00	14.00	0.00
30	4	6.83	1.18	2.83	1.43	9.66	2.61
	8	8.83	0.94	6.50	0.71	15.33	1.65
	12	11.00	1.78	7.50	0.41	18.50	2.19
40	4	10.67	1.18	7.00	0.41	17.67	1.59
	8	15.50	1.47	7.83	0.47	23.33	1.94
	12	14.50		8.50		23.00	

<sup>a</sup> Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>. <sup>b</sup> Percentange composition with respect to total amount of anisonitrile and Ar-containing alkyne products.

### Attempted NACM With Other Mo Complexes

General Procedure: [Mo] (20.0 mg), anisonitrile (10 equiv), and an internal standard of 1,3,5-trimethoxybenzene were dissolved in bromobenzene-*d*<sub>5</sub> (5.0 mL) at a concentration of 40 mg mL<sup>-1</sup>, then the solution was transferred to a J. Young tube. Then 1-phenyl-1-butyne (10 equiv) was introduced *via* syringe and the overlying atmosphere was removed *in vacuo*. The reaction was heated at 180-185 °C and monitored by <sup>1</sup>H NMR spectroscopy. ACM products were observed in all cases, but are indicated only for those complexes that have not been previously been shown to catalyze ACM at  $\leq 90$  °C.

**NMo(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>(NHMe<sub>2</sub>) (12).** Following the general procedure: **12** (19.6 mg, 0.029 mmol), anisonitrile (39.3 mg, 0.30 mmol), and 1-phenyl-1-butyne (41.4 μL, 0.29 mmol). After 20 h, no NACM products were observed with 2,6-diisopropylphenol being the only phenolic species present.

**NMo(OSiPh<sub>3</sub>)<sub>3</sub>(NHMe<sub>2</sub>) (5-NHMe<sub>2</sub>).** Following the general procedure: **5-NHMe<sub>2</sub>** (20.3 mg, 0.021 mmol), anisonitrile (26.8 mg, 0.20 mmol), and 1-phenyl-1-butyne (29.0 μL, 0.20 mmol). After 20 h, no NACM products were observed. The fate of **5-NHMe<sub>2</sub>** was unclear, and so additional 1-phenyl-1-butyne (87.0 μL, 0.61 mmol) was added and the reaction heated at 90 °C. After 1 h, no additional ACM products were observed, indicating decomposition of **5-NHMe<sub>2</sub>**.

**NMo(OSiPh<sub>3</sub>)<sub>3</sub>(py) (5-py).** Following the general procedure: **5** (20.0 mg, 0.021 mmol), pyridine-d<sub>5</sub> (1.90 μL, 0.024 mmol), anisonitrile (29.4 mg, 0.22 mmol), and 1-phenyl-1-butyne (30.4 μL, 0.21 mmol). After 12 h, a 14 % conversion to NACM products was observed.

**NMo(OSiPh<sub>2</sub><sup>t</sup>Bu)<sub>3</sub> (16).** Following the general procedure: **16** (80.0 μL of a 0.25 mg μL<sup>-1</sup> stock solution in C<sub>6</sub>D<sub>6</sub>, 0.023 mmol), anisonitrile (30.1 mg, 0.26 mmol), and 1-phenyl-1-butyne (32.4 μL, 0.23 mmol). After 8 h, no NACM products were observed but ACM had occurred to give a mixture of 1-phenyl-1-butyne (54 %), diphenylacetylene (23 %), and 3-hexyne (23 %); 83 % of **16** remained.

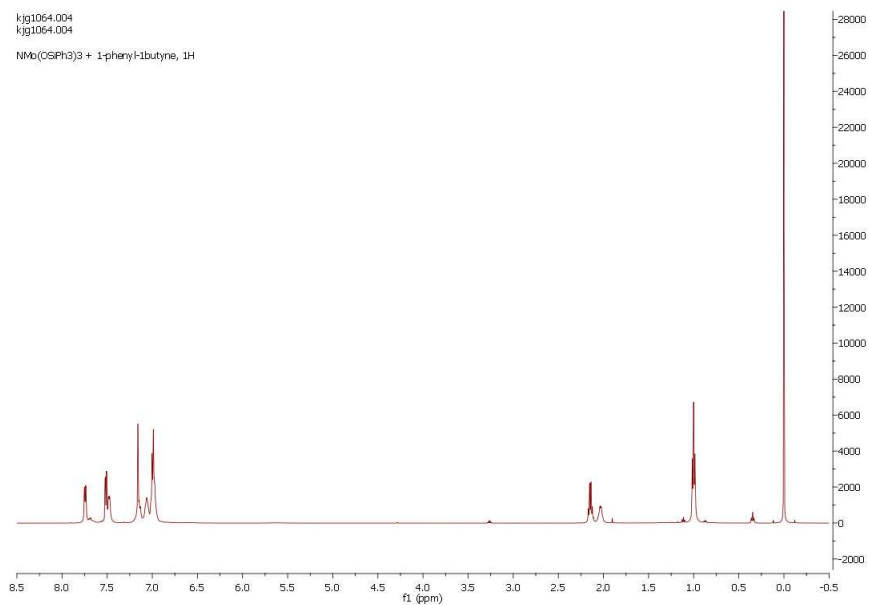
**NMo(O<sup>t</sup>Bu)<sub>3</sub> (6).** Following the general procedure: **6** (20.5 mg, 0.062 mmol), anisonitrile (80.8 mg, 0.61 mmol), and 1-phenyl-1-butyne (86.0  $\mu$ L, 0.61 mmol). After 4 h, no NACM products were observed, but ACM had occurred to give a mixture of 1-phenyl-1-butyne (50 %), diphenylacetylene (25 %), and 3-hexyne (25 %). After 16 h, no NACM was observed and **6** had decomposed.

**NMo(OCMe<sub>2</sub>CF<sub>3</sub>)<sub>3</sub> (7).** Following the general procedure: **7** (20.6 mg, 0.042 mmol), anisonitrile (56.9 mg, 0.43 mmol), and 1-phenyl-1-butyne (58.0  $\mu$ L, 0.41 mmol). After 4 h, no NACM products were observed, but 82 % **7** remained and ACM had occurred to give a mixture of 1-phenyl-1-butyne (50 %), diphenylacetylene (25 %), and 3-hexyne (25 %). After 16 h, no NACM was observed and 51 % **7** remained.

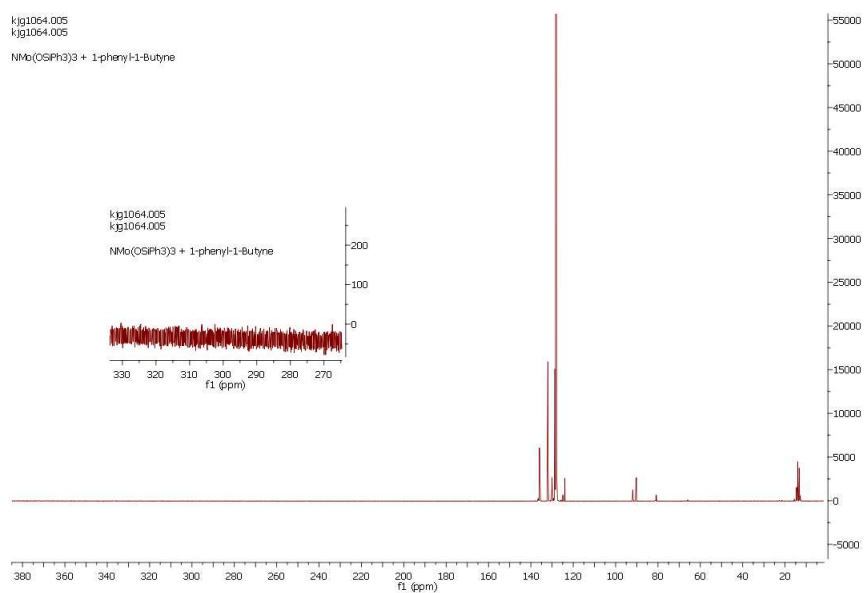
**NMo(OC(CF<sub>3</sub>)<sub>2</sub>Me)<sub>3</sub> (3).** Following the general procedure: **3** (22.0 mg, 0.034 mmol), anisonitrile (40.7 mg, 0.41 mmol), and 1-phenyl-1-butyne (40.0  $\mu$ L, 0.28 mmol). After 4 h, no NACM was observed and **3** had decomposed.

**NMo(OC(CF<sub>3</sub>)<sub>3</sub>)(NCMe) (4).** Following the general procedure: **4** (20.7 mg, 0.024 mmol), anisonitrile (31.2 mg, 0.23 mmol), and 1-phenyl-1-butyne (33.0  $\mu$ L, 0.23 mmol). After 4 h, no NACM was observed and **4** had decomposed.

**Reaction between 5 and 1-phenyl-1-butyne.** In a J. Young tube, a solution of **5** (7.2 mg, 0.0077 mmol) and 1-phenyl-1-butyne (22  $\mu$ L, 0.16 mmol) in  $C_6D_6$  was heated in a 90  $^{\circ}C$  for 16 h. Upon cooling,  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra were recorded.

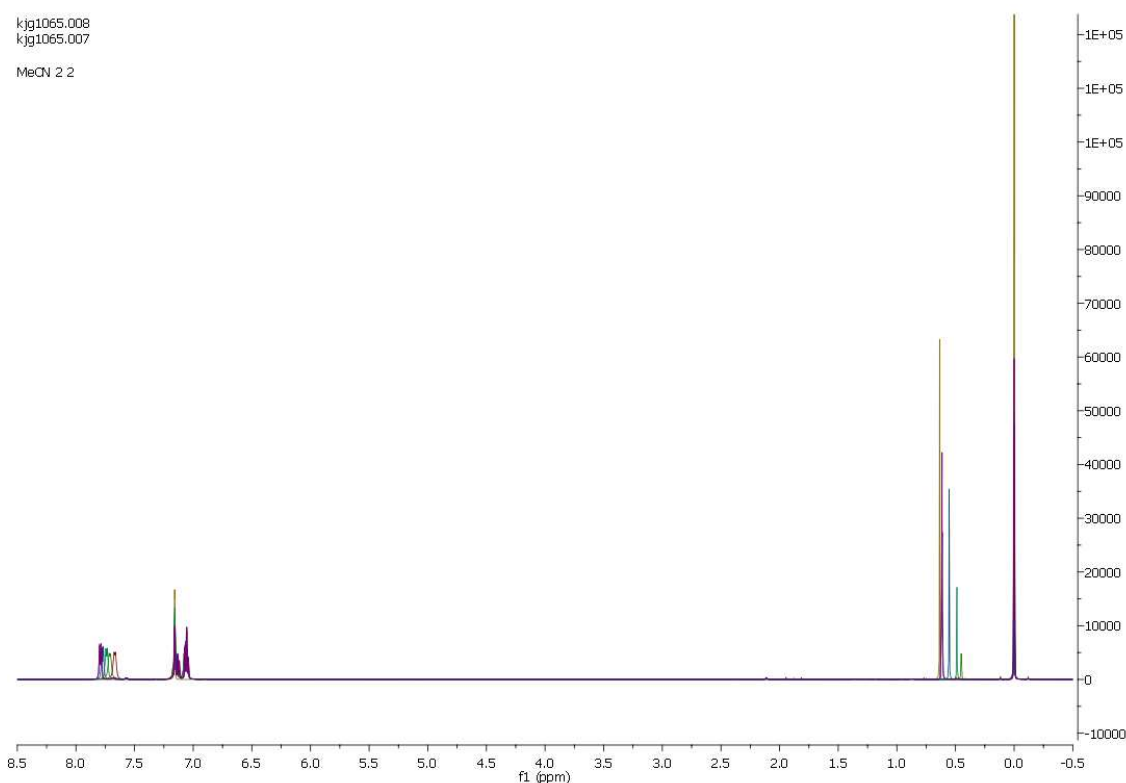


**Figure S1.  $^1H$  NMR of reaction between 5 and 1-phenyl-1-butyne.**



**Figure S2.  $^{13}C\{^1H\}$  NMR of reaction between 5 and 1-phenyl-1-butyne.**

**Reaction of **5** with MeCN.** An  $^1\text{H}$  NMR spectrum of complex **5** in  $\text{C}_6\text{D}_6$  was taken. The  $^1\text{H}$  NMR spectrum was recorded for sequential addition of 1, 2, 5, 10 and 20 Eq of NCMe. A clear change in chemical shift in both the NCMe and the signals corresponding to complex **5** can be seen with addition of NCMe.



**Figure S3.  $^1\text{H}$  NMR of reaction between **5** and MeCN.**

**Attempted N-atom exchange with **5**.** Complex **5** (20mg, 0.02 mmol) and anisonitrile (5 equiv, 14 mg, 0.1 mmol) were added to a solution of  $^{15}\text{NCMe}$  (14 equiv, 16  $\mu\text{L}$ ) in  $\text{C}_6\text{D}_6$ . The  $^1\text{H}$  NMR spectrum and  $^{15}\text{N}$  NMR spectrum were recorded. No change in the NMR spectrum from  $^{15}\text{NCMe}$  alone was observed for  $^{15}\text{N}$  NMR. The solution was then heated to  $80^\circ\text{C}$  for 60 hours with no change in the  $^{15}\text{N}$  NMR spectrum observed. It can therefore be concluded that no metathesis of  $^{15}\text{NCMe}$  with the metal centre had occurred.