Journal of Organometallic Chemistry 708-709 (2012) 1–9

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Catalytic alkyne metathesis and stoichiometric metal–alkylidyne formation from N≡Mo(OR)$_3$ complexes promoted by Lewis acids

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ARTICLE INFO

Article history:
Received 1 May 2011
Received in revised form
30 July 2011
Accepted 1 August 2011

Dedicated to Professor Kenneth G. Caulton on the occasion of his 70th birthday.

Keywords:
Alkyne
Metathesis
Molybdenum
Nitride
Alkylidyne
Lewis acid

ABSTRACT

Nitride complex N≡Mo(OCMe$_2$CF$_3$)$_3$ is synthesized in 78% yield on a multigram scale. Although the irreversible but sluggish conversion of terminal molybdenum–nitride complexes N≡Mo(OCMe(CF$_3$)$_2$)$_3$ (**1**) and N≡Mo(OC(CF$_3$)$_3$)$_3$(NCMe) (**2**) to their propylidyne analogs EtC≡Mo(OR)$_3$(DME) (OCMe(CF$_3$)$_2$ (**3**), OC(CF$_3$)$_3$ (**4**)) via metathesis with 3-hexyne occurs, the analogous reaction with N≡Mo(OR)$_3$ (OR= OCMe$_2$CF$_3$ (**5**), OCMe$_3$ (**6**)) complexes does not occur under similar reaction conditions. However, the kinetic barrier to alkylidyne formation from **5** and **6** with internal alkynes can be overcome through the addition of simple Lewis acids, including MgBr$_2$, MgI$_2$ and BPh$_3$ in specific instances. Although this typically leads to accelerated decomposition of the alkylidyne complex so formed, the combination of metal–nitride complex plus exogenous Lewis acid frequently leads to alkyne metathesis of the test substrates 1-phenyl-1-propyne and 1-phenyl-1-butyne under milder conditions than possible in the absence of Lewis acid, in some cases at room temperature. The interaction of solvent, ancillary alkoxide ligands, and Lewis acid is complex and was not predicted a priori. New benzylidyne complexes 4-MeOC$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(MeOC$_6$H$_4$CN) (22%), 4-Ph–C$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(4-PhC$_6$H$_4$CN) (46%) were isolated in low yield via the nitride-to-alkylidyne route upon reaction with suitable diarylalkynes. Several related alkylidyne complexes were formed but could not be separated cleanly from the alkyne reagents used.

1. Introduction

The conversion of **1** to **3** via metathesis with 3-hexyne is one of the most facile methods for preparing a molybdenum–alkylidyne complex in good yield (Scheme 1) [1]. The analogous metathesis of **2** with 3-hexyne to afford **4** can be effected at a lower temperature (Scheme 1). However, decomposition of **4** during concentration of the reaction mixture has hindered its isolation. The *in situ* decomposition of **4** is enhanced when the reaction is conducted at the 95 °C originally reported. With a limited number of examples of the nitride-to-alkylidyne moiety conversion at molybdenum [1,2], the potential breadth of this methodology has yet to be fully exploited.

The incorporation of more economical OCMe$_2$CF$_3$ and OCMe$_3$ ligands would enhance the scope of this nitride-to-alkylidyne complex conversion. Unfortunately, conversion of **5** or **6** to EtC≡Mo(OR)$_3$ complexes via metathesis with 3-hexyne has not been achieved. The potential pre-catalysts **5** and **6** were treated with 20 equiv of 1-phenyl-1-propyne at 95 °C in order to probe for any alkyne-metathesis activity. The formation of an equilibrium mixture of diphenylacetylene, 1-phenyl-1-propyne, and 2-butyne in the presence of **5** indicated that at least trace conversion to an alkylidyne complex occurred (Scheme 2). However, the rate of alkyne metathesis with **5** was slow, requiring 9 days to achieve equilibrium, and no alkylidyne complexes were directly observed. No successful metathesis was observed by ^{1}H NMR spectroscopy with **6** under these conditions.

At this point we sought to enhance the rate of alkylidyne complex formation from a nitride precursor. The earliest homogeneous alkyne metathesis system consisted of Mo(CO)$_6$, and phenol [3]. Modifications of this system have been reported by Bunz, Grela, and Mori [4,5]; the phenol exerts a substantial influence on catalyst performance [6–8]. Although the active species in these reaction mixtures has yet to be identified, it is frequently assumed to be a Schrock-type alkylidyne complex [9–11].

Inspired by this work and the potential role that a Lewis acid such as phenol has on alkyne metathesis, we decided to investigate

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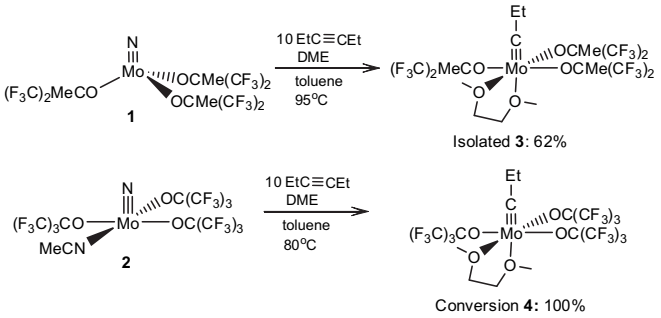
0022-328X/$ – see front matter © 2012 Published by Elsevier B.V.
doi:10.1016/j.jorganchem.2011.08.001



Scheme 1. Syntheses of **3** and **4** via metathesis of N≡Mo(OR)$_3$ complexes with 3-hexyne.

the influence of simple Lewis acids on the conversion of N≡Mo(OR)$_3$ into RC≡Mo(OR)$_3$ complexes [12]. There are three potentially favorable interaction modes of the Lewis acids with our nitride pre-catalysts (Fig. 1). First, the Lewis acid could bind directly to the nitride moiety (**A**). This is observed when B(C$_6$F$_5$)$_3$ is used [2], and should affect the rate of nitride-to-alkylidyne conversion, but not subsequent alkyne metathesis. Molybdenum–alkylidyne complexes are in general more difficult to synthesize than their tungsten counterparts, but several efficient syntheses of benzylidyne complexes of molybdenum and tungsten via low- and high-oxidation-state precursors have been reported recently [11,13–18]. Alternatively, coordination of the Lewis acid to the alkoxide ligand could occur (**B**). Lastly, if an additional coordinating ligand is present in the coordination sphere of a precatalyst such as a molybdenum nitride complex, the Lewis acid could activate the precursor by abstracting or trapping this ligand upon its dissociation, as noted in the reaction of recently reported N≡Mo(OSiPh$_3$)$_3$(py) [18] with one equivalent of B(C$_6$F$_5$)$_3$ (**C**) [2].

The first two Lewis acid binding modes are equivalent to decreasing the pKa of the conjugate acid of the ancillary ligand. Comparison of the metal centers of an alkylidyne and a nitride complex with same ancillary ligand set reveals that a lesser positive charge is present on the alkylidyne center [19]. Thus, alkylidyne complex formation should become more favorable relative to the nitride as the electron-donating capacity of the ancillary ligands decreases (Fig. 2). Furthermore, theoretical calculations and experimental data have demonstrated that altering the electron donating-ability of the alkoxide ligands influences the rate of alkyne metathesis dramatically [20–22]. These studies indicated that introduction of a poor electron-donor ancillary ligand stabilizes the transition state for metalacyclobutadiene formation. Thus, enhanced rates of alkyne metathesis should occur if the Lewis acid coordinates to the alkoxide of the alkylidyne complex due to the resulting increased Lewis acidity of the metal center.

2. Experimental section

2.1. General procedures

All reactions were performed in an atmosphere of dinitrogen, either in a nitrogen-filled MBRAUN Labmaster 130 glove box or by using standard air-free techniques. ^{1}H NMR spectra were recorded at 499.909 MHz, 399.967 MHz on a Varian Inova 400 spectrometer or 300.075 MHz on a Varian Inova 300 spectrometer and referenced to the residual protons in toluene-d_8 (2.09 ppm), $CDCl_3$ (7.26 ppm), CD_2Cl_2 (5.33 ppm), and C_6D_6 (7.15 ppm). ^{19}F NMR spectra were recorded at 282.384 MHz on a Varian Inova 300 spectrometer or 376.303 MHz on a Varian Inova 400 spectrometer and were referenced to an external standard of $CFCl_3$ in $CDCl_3$ (0.00 ppm). ^{13}C NMR spectra were recorded at 100.596 MHz on a Varian Inova 400 spectrometer and were referenced to naturally abundant ^{13}C nuclei in CD_2Cl_2 (54.00 ppm). GC/MS data were collected on a Shimadzu GCMS-QP5000 with a Restek XTI-5 phase column (30 m, 0.25 I.D., 0.25 D. F.). EI MS data were collected on a VG (Micromass) 70-250-S Magnetic sector mass spectrometer.

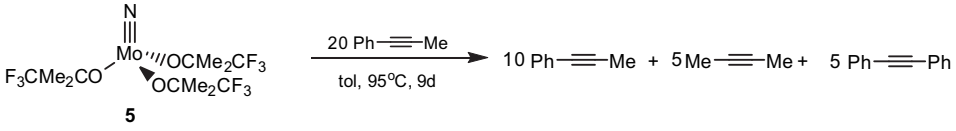
2.2. Materials and methods

All solvents used were dried and deoxygenated by the method of Grubbs [23]. Bis(4-methoxyphenyl)acetylene [24,25], $VCl_3(thf)_3$ [26], N≡Mo(OCMe$_3$)$_3$ (**6**) [27], N≡Mo(OCMe(CF$_3$)$_2$)$_3$ (**1**) [28], and N≡Mo(OC(CF$_3$)$_3$)$_3$(NCMe) (**2**) [28], were prepared according to literature procedures. Mesitylene, diphenylacetylene, and chlorotitanium tri-isopropoxide were obtained from Acros. 3-hexyne, 1-phenyl-1-butyne, and 1-phenyl-1-propyne were obtained from GFS Chemicals and dried over 4 Å molecular sieves for at least 24 h. Magnesium bromide, magnesium iodide, and hydrochloric acid (2.0 M) in Et$_2$O were obtained from Aldrich. Zirconium (IV) chloride and copper (II) chloride were obtained from Strem Chemicals, Inc. 4-bromobiphenyl was obtained from TCI Organic Chemicals. NMR solvents were obtained from Cambridge Isotope Laboratories and were dried over 4 Å molecular sieves for at least 24 h. All reagents were used as received unless otherwise noted.

2.3. Nitride-to-alkylidyne complex syntheses

2.3.1. Synthesis of N≡Mo(OCMe$_2$CF$_3$)$_3$ (**5**)

$MoCl_4(NCMe)_2$ (3.0 g, 9.4 mmol) was slurried in 100 mL acetonitrile. NaN_3 (735 mg, 11.3 mmol, 1.20 equiv) was added to the suspension. [*Warning!* Sodium azide is potentially explosive and is used here in 20% excess. Care should be taken not to heat the crude material, particularly during subsequent solvent removal, as some NaN_3 remains. This must be disposed of properly. As an alternative, 0.99 equiv NaN_3 may be used, though the isolated yield of **5** decreased to 65% in one attempt under these conditions. The mixture was capped with a needle-pierced septum and left to stir for 2 h at 30 °C. The acetonitrile was removed from the resulting dark red mixture *in vacuo*. The resultant solid residue was triturated with 10 mL of toluene before it was slurried in 100 mL toluene. Solid $LiOMe_2CF_3$ (3.85 g, 28.7 mmol, 3.05 equiv) was added to the toluene solution and the mixture was left to stir for 12 h at 30 °C. The mixture was then heated and filtered through celite using excess toluene. The solvent was removed *in vacuo* and the resulting residue was redissolved in ca. 18 mL boiling toluene and cooled to −35 °C overnight. Upon vacuum filtration of the resulting mixture, 3.62 g (7.37 mmol, 78.4%) of pale brown crystals were recovered. ^{1}H NMR (C_6D_6): δ 1.41 (s, OC(CH_3)$_2$CF$_3$). ^{19}F NMR (C_6D_6):



Scheme 2. Alkyne metathesis with **5**.

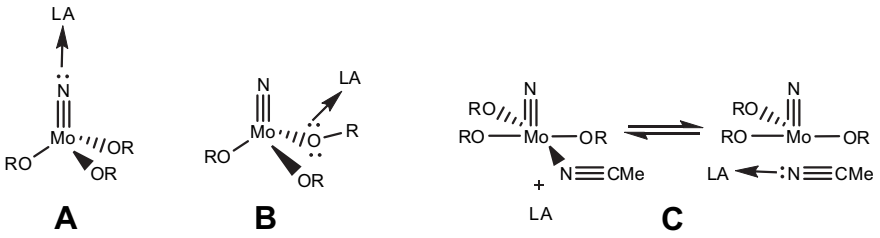


Fig. 1. Potential Lewis acid binding modes.

δ −82.99 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 126.18 (q, CF_3, J_{C-F} = 284.59 Hz), 82.52 (q, CH_3, J_{C-F} = 29.69 Hz), 22.91 (s, $OC(CH_3)_2CF_3$). Anal. Calc for $N{\equiv}MoO_3C_{12}H_{18}F_9$: C, 29.34; H, 3.70; N, 2.85. Found: C, 28.75; H, 3.62; N, 3.03.

2.3.2. Synthesis of EtC≡Mo(OCMe(CF$_3$)$_2$)$_3$(NCEt) (**7**)

Complex **1** (10.0 mg, 0.0153 mmol) was dissolved in C_6D_6 (0.5 mL). Then 3-hexyne (17.4 μL, 0.153 mmol, 10 equiv) was added to the solution via syringe. The solution was frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated to 95 °C for 29 h. At this point the reaction mixture consisted of **7** (80%) and a decomposition product (unidentified). The volatiles were removed *in vacuo* from the reaction mixture. The resulting residue was then reconstituted in C_6D_6. At this point insoluble material was present in the reaction mixture along with increased evidence of decomposition with **7** only accounting for 63% of the ^{19}F NMR spectrum. ^1H NMR (400 MHz, C_6D_6): δ 2.44 (q, 2H, ≡CH_2CH$_3$, J = 7.6 Hz), 1.55 (s, 9H, $OC(CH_3)_2CF_3$), 1.10 (s br, 2H, N≡CH_2CH$_3$), 0.56 (t, 3H, ≡CH$_2$$CH_3$, J = 7.6 Hz), 0.34 (t, 3H, N≡CH$_2$$CH_3$, J = 7.6 Hz) ^1H NMR (400 MHz, CD_2Cl_2, −40 °C): δ 3.15 (q br, 2H, ≡CH_2CH$_3$, J = 7.5 Hz), 2.62 (q br, 2H, N≡CH_2CH$_3$, J = 7.5 Hz), 1.81 (s, 9H, $OC(CH_3)_2CF_3$), 1.32 (t br, 3H, N≡CH$_2$$CH_3$, J = 7.5 Hz), 1.02 (t br, 3H, ≡CH$_2$$CH_3$, J = 7.5 Hz). ^{19}F NMR (300 MHz, C_6D_6): δ −77.67 (s, CF_3). EI/MS $[m/z]^+$: 730.0 (EtC≡Mo(OCMe(CF$_3$)$_2$)$_3$).

2.3.3. Synthesis of EtC≡Mo(OC(CF$_3$)$_3$)$_3$(NCEt) (***8***)

Complex **2** (100.0 mg, 0.117 mmol) was dissolved in toluene (3 mL). 3-hexyne (26.5 μL, 0.234 mmol, 2 equiv) was added via syringe to the solution. The solution was then heated to 75 °C for 12 h. Upon removal of volatiles *in vacuo* a few orange crystals of **8** crystallized on the side of the reaction vial. ^1H NMR (400 MHz, C_6D_6): δ 2.79 (q, 2H, ≡CH_2CH$_3$, J = 7.6 Hz), 0.62 (t, 3H, ≡CH$_2$$CH_3$, J = 7.6 Hz), 0.35 (t, 3H, N≡CH$_2$$CH_3$, J = 7.6 Hz). ^1H NMR (400 MHz, toluene-d_8, −20 °C): 2.83 (q br, 2H, ≡CH_2CH$_3$, J = 7.0 Hz), 1.08 (q br, 2H, N≡CH_2CH$_3$, J = 7.6 Hz), 0.67 (t, 3H, ≡CHCH_3, J = 7.0 Hz), 0.39 (t, 3H, N≡CH$_2$$CH_3$, J = 7.4 Hz). ^{19}F NMR (300 MHz, C_6D_6): −72.44 (s, CF_3). EI/MS $[m/z]^+$: 843.9 (EtC≡Mo(OC(CF$_3$)$_3$)$_3$).

2.3.4. Synthesis of PhC≡Mo(OCMe(CF$_3$)$_2$)$_3$(DME)

Complex **1** (1.00 g, 1.53 mmol) and diphenylacetylene (2.73 g, 15.3 mmol, 10 equiv) were dissolved in toluene (50 mL). Then 3-hexyne (522 μL, 4.59 mmol, 3 equiv) was added to the reaction mixture via syringe. The mixture was sealed and heated to 95 °C for 24 h. The reaction mixture was filtered through celite and the celite was washed with pentane (40 mL). The volatiles were then removed *in vacuo*. The reaction mixture was taken up in toluene/pentane (16 mL) and DME (159 μL, 1.53 mmol, 1 equiv) was added. The mixture was then cooled in the freezer. Following repeated recrystallizations PhC≡Mo(OCMe(CF$_3$)$_2$)$_3$(DME) (158 mg, 0.205 mmol, 20%) was isolated. Further isolation could not be achieved through recrystallization. Characterization data agreed with the literature [29].

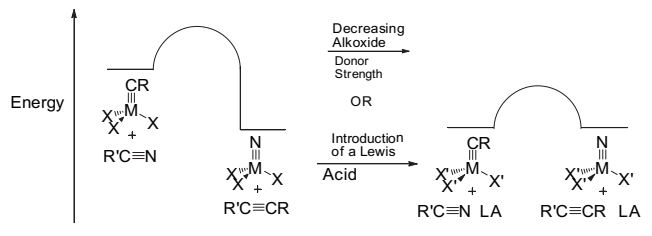


Fig. 2. Qualitative influence of alkoxide and Lewis acids on relative stabilities of nitride and alkylidyne complexes.

2.3.5. Synthesis of 4-PhC$_6$H$_4$C≡Mo(OCMe(CF$_3$)$_2$)$_3$(4-PhC$_6$H$_4$CN) (***10***)

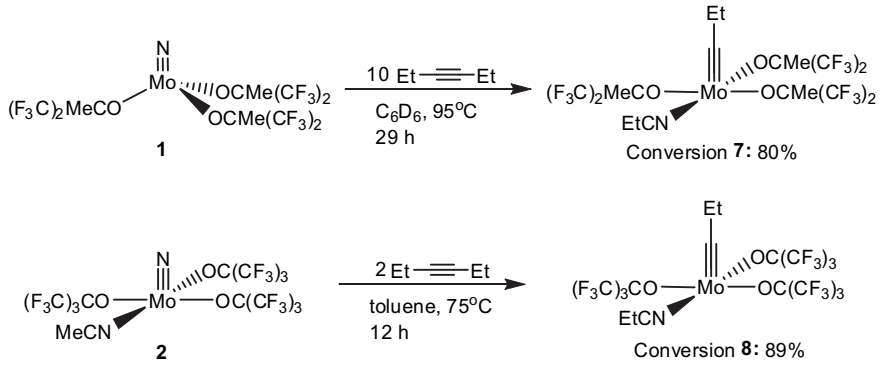
Complex **1** (5.0 mg, 0.0077 mmol) and bis(4-biphenyl)acetylene (25.3 mg, 0.0766 mmol, 10 equiv) were slurried in toluene-d_8 (0.5 mL). Then 3-hexyne (1.9 μL, 0.023 mmol, 3 equiv) was added via syringe to the reaction mixture. The reaction mixture was heated to 95 °C for 3 d. At this point the reaction mixture consisted of **10** (51%) and **1** (39%). Further heating of the reaction mixture for 1 d only resulted in an additional 1% formation of **10** (52%).

2.3.6. Synthesis of 4-MeOC$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(4-MeOC$_6$H$_4$CN)

Complex **2** (500.0 mg, 0.5840 mmol) and bis(4-methoxyphenyl) acetylene (339.2 mg, 1.424 mmol, 2.438 equiv) were dissolved in toluene (25 mL). The reaction mixture was heated to 60 °C for 6 d. The reaction volume was reduced by half and the mixture was heated to 60 °C for an additional 2 d. At this point, the reaction mixture was 84% 4-MeOC$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(MeOC$_6$H$_4$CN), 7% **2**, and 9% of a decomposition product. The volatiles were removed *in vacuo* and the reaction mixture was extracted with pentane (30 mL) and filtered. The resulting filtrate was extracted with pentane (10 mL) and the volatiles were removed *in vacuo*. The resulting material was dissolved in Et$_2$O/pentane (5 mL) and cooled to −35 °C. A purple powder of 4-MeOC$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(MeOC$_6$H$_4$CN) was isolated via filtration (133.2 mg, 0.1075 mmol, 22%). ^1H NMR (400 MHz, C_6D_6): δ 7.23 (d, 2H, ArH, J = 9.0 Hz), 7.06 (d, 2H, ArH, J = 9.0 Hz), 6.35 (d, 2H, ArH, J = 9.0 Hz), 6.15 (d, 2H, ArH, J = 9.0 Hz), 3.04 (s, 3H, OMe), 2.95 (s, 3H, OMe). ^{19}F NMR (300 MHz, C_6D_6): −72.48 (s, CF_3). $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2): δ 321.94 (s, Mo≡C), 165.95 (s, ArC), 162.20 (s, ArC), 137.52 (s, ArC), 135.54 (s, ArC), 133.23 (s, ArC), 133.14 (s, ArC), 121.60 (q, $OC(CF_3)_3$, J_{C-F} = 293.2 Hz), 116.15 (s, ArC), 113.22 (s, ArC), 101.83 (s, ArC) 99.38 (s, CN), 87.02 (m, $OC(CF_3)_3$), 56.44 (s, OMe), 55.86 (s, OMe).

2.3.7. Synthesis of 4-PhC$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(4-PhC$_6$H$_4$CN)

Complex **2** (5.0 mg, 0.0058 mmol) and bis(4-biphenyl)acetylene (19.3 mg, 0.0584 mmol, 10 equiv) were slurried in C_6D_6 (0.5 mL). The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The mixture was then heated to 95 °C for 3 d. At this point the reaction mixture consisted of 88% 4-Ph−C$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(4-PhC$_6$H$_4$CN). **Scale-Up.** Complex **2** (1.0 g, 1.17 mmol) and bis(4-biphenyl)acetylene (2.88 g, 8.76 mmol,



Scheme 3. Formation of **7** and **8** via metathesis of N≡Mo(OR)$_3$ complexes with 3-hexyne.

7.5 equiv) were slurried in toluene (50 mL). The reaction mixture was then heated at 95 °C for 3 d. The mixture and the resulting white precipitate were washed with toluene (40 mL) and then pentane (10 mL). The volatiles were removed *in vacuo* from the filtrate. The resulting material was extracted with toluene and filtered. The resulting filtrate was reduced to dryness and dissolved in 1:1 Et_2O/hexane (10 mL) and cooled to −35 °C. The resulting tan powder was filtered and the filtrate was taken up in toluene/hexane (7 mL) and cooled to −35 °C. A dark red-brown powder of 4-Ph−C_6H_4C≡Mo(OC(CF_3)$_3$)$_3$(4-PhC_6H_4CN) formed (508.9 mg, 0.444 mmol, 38%). ^{19}F NMR (400 MHz, C_6D_6): −72.3 (s, CF_3). ^{1}H NMR (400 MHz, C_6D_6): 7.40 (d, J = 8.2 Hz), 7.00−7.278 (m), 7.01 (d, J = 7.0 Hz). EI/MS [m/z]$^+$: 968.0, 4-PhC_6H_4C≡Mo(OCMe(CF_3)$_2$)$_3$.

2.4. General protocol for Lewis acid testing

2.4.1. General procedure with **5**

Complex **5** was dissolved in CD_2Cl_2 (20.4 mM). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was monitored via ^{1}H NMR spectroscopy at 40 °C.

2.4.2. General procedure with **6**

Complex **6** was dissolved in C_6D_6 (30.4 mM). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was monitored via ^{1}H NMR spectroscopy at 80 °C.

2.4.3. General procedure with **1**

Complex **1** was dissolved in $CDCl_3$ (1.0 mL). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction was monitored via ^{1}H NMR spectroscopy at room temperature.

2.4.4. General procedure with **2**

Complex **2** was dissolved in C_6D_6 (1.0 mL). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction was monitored via ^{1}H NMR spectroscopy at room temperature.

2.5. Solvent studies for Lewis acid testing

2.5.1. General procedure with **1**

Complex **1** (5.0 mg, 0.0077 mmol) was dissolved in an appropriate solvent (500 μL). Then 1-phenyl-1-propyne (18.9 μL, 0.153 mmol, 20 equiv) and an internal standard of mesitylene were added via syringe. The reaction was monitored at room temperature.

2.5.2. General procedure with **2**

Complex **2** (5.0 mg, 0.0058 mmol) was dissolved in an appropriate solvent (500 μL). Then 1-phenyl-1-propyne (14.4 μL, 0.117 mmol, 20 equiv) and an internal standard of mesitylene were added via syringe. The reaction was monitored at room temperature.

2.5.3. General procedure with **5**

Complex **5** (10.0 mg, 0.0204 mmol) was dissolved in an appropriate solvent (1 mL). Then 1-phenyl-1-butyne (57.9 μL, 0.407 mmol, 20 equiv) and an internal standard of mesitylene were added via syringe. This solution was transferred to a vial containing

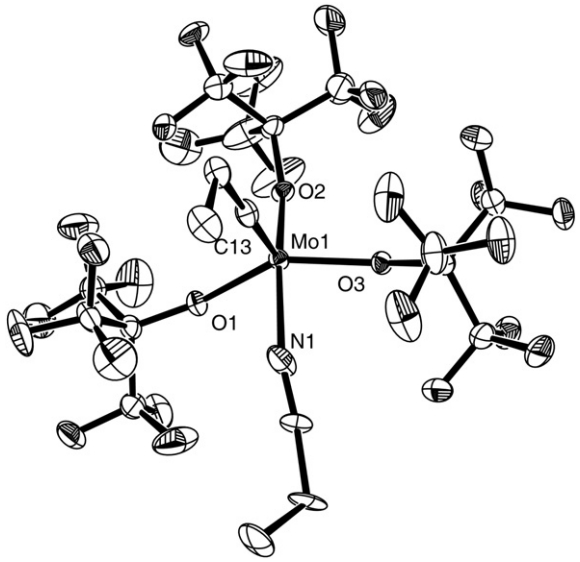


Fig. 3. . 50% Thermal ellipsoid plot of **8**.

Table 1
Selected Bond Lengths and Angles for **8**.

Complex **8**			
Bond distances (Å)			
Mo–C(13)	1.722(2)	Mo–O(3)	1.9528(16)
Mo–O(1)	1.9604(16)	Mo–N(1)	2.182(2)
Mo–O(2)	1.9390(16)		
Bond angles (deg)			
C(13)–Mo–O(1)	105.30(9)	O(2)–Mo–O(3)	94.16(7)
C(13)–Mo–O(2)	105.16(9)	O(1)–Mo–N(1)	81.47(8)
C(13)–Mo–O(3)	104.72(9)	O(3)–Mo–N(1)	83.30(8)
C(13)–Mo–N(1)	91.30(11)	O(1)–Mo–O(2)	92.10(7)

magnesium bromide (7.5 mg, 0.041 mmol, 2 equiv). The resulting reaction mixture was then placed in a J. Young tube. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was then monitored at 60 °C.

2.5.4. General procedure with **6**

Complex **6** (5.0 mg, 0.015 mmol) was dissolved in an appropriate solvent (500 μL). Then 1-phenyl-1-propyne (37.5 μL, 0.304 mmol, 20 equiv) and an internal standard of mesitylene were added via syringe. This solution was transferred to a vial containing magnesium bromide (5.6 mg, 0.030 mmol, 2 equiv). The resulting reaction mixture was then placed in a J. Young tube. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was then monitored at 60 °C.

2.6. Alkyne dependence studies

Complex **5** was dissolved in CD_2Cl_2 (20.4 mM). 1-phenyl-1-butyne (20 equiv) or 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was monitored via ^{1}H NMR spectroscopy at 40 °C.

2.7. X-ray crystallography

Orange needles of **8** were grown from a toluene solution at 25 °C. A crystal of dimensions 0.32 × 0.14 × 0.11 mm mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(2) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 3490 frames were collected with a scan width of 0.5° in ω and 0.45° in φ with an exposure time of 15 s/frame. The integration of the data yielded a total of 90081 reflections to a maximum 2θ value of 60.20° of which 7850 were independent and 7227 were greater than $2\sigma(I)$. The final cell constants were based on the xyz centroids of 9987 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package, using the space group P2(1)/n with $Z = 4$ for the formula $C_{18}H_{10}F_{27}NO_3Mo$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The propionitrile ligand is disordered over two positions. Full matrix least-squares refinement based on F^2 converged at $R1 = 0.0402$ and $wR2 = 0.1040$ [based on $I > 2\sigma(I)$], $R1 = 0.0436$ and $wR2 = 0.1069$ for all data.

Table 2
Crystallographic Data for Complex **8**.

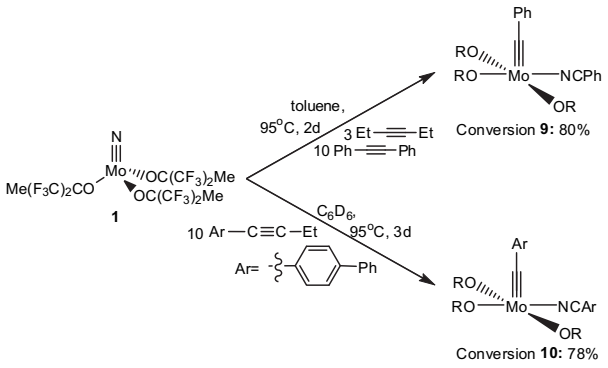
Complex **8**	
Formula	$C_{18}H_{10}F_{27}O_3NMo$
FW	897.21
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.9445(9)
b (Å)	18.1387(15)
c (Å)	15.0623(12)
α (deg)	90
β (deg)	110.8650(10)
γ (deg)	90
V (Å)	2794.1(4)
Z	4
Radiation (Ka, Å)	0.7103
T (K)	108(2)
D_{calcd} (Mg m^{-3})	2.133
m_{calcd} (mm^{-1})	0.676
F_{000}	1736
$R1$	0.0402
w$R2$	0.1040
GOF	1.062

3. Results and discussion

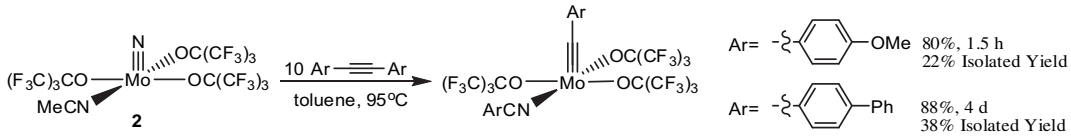
3.1. Nitride-to-alkylidyne complex conversion with $OCMe(CF_3)_2$ and $OC(CF_3)_3$ ligands

Due to the continued decomposition of **4** during attempted isolation in the presence of DME, the nitride-to-alkylidyne complex conversion was investigated in the absence of DME. Spectroscopic evidence for the formation of EtC≡Mo(OR)$_3$(NCEt) (OR= $OCMe(CF_3)_2$ (**7**), $OC(CF_3)_3$ (**8**)) was found (Scheme 3). Upon removal of the volatiles, a similar decomposition of the reaction mixtures has prevented isolation of **7** and **8** in good yield. The identity of the decomposition product(s) is under investigation.

Further reaction of the **7** and **8** upon concentration under reduced pressure is not surprising, as ^{1}H NMR spectroscopy indicates that bound and unbound propionitrile exchange on the NMR time scale in both **7** and **8**. Upon cooling solutions of **7** and **8** to −40 °C and −20 °C respectively, distinct quartets that correspond to bound propionitrile appear in the ^{1}H NMR spectra (S1, S2, S3, and S4). Isolation of a small sample of **8** in crystalline form was achieved as the reaction mixture was concentrated under vacuum. A thermal ellipsoid plot of **8** (Fig. 3) reveals an approximately square pyramidal geometry about molybdenum (Table 1) with propionitrile coordinated *trans* to one alkoxide ligand. Structure refinement data are collected in Table 2.



Scheme 4. Formation of **9** and **10** from **1**.



Scheme 5. Formation of ArC≡Mo(OC(CF$_3$)$_3$)$_3$(NCAr) complexes from **2**.

3.2. Nitride-to-benzylidyne complex conversion with OCMe(CF$_3$)$_2$ and OC(CF$_3$)$_3$ ligands

Methods for the preparation of ArC≡Mo(OR)$_3$ complexes from **1** and **2** were explored next (Scheme 4). Direct formation of PhC≡Mo(OCMe(CF$_3$)$_2$)$_3$(NCPh) (**9**) via metathesis of **1** with diphenylacetylene was not observed by ^{1}H NMR spectroscopy, even upon heating to 90 °C for 2 days. In contrast, treatment of **1** with 3 equiv of 3-hexyne and 10 equiv of diphenylacetylene resulted in 80% conversion to **9**. Difficulty in separating diphenylacetylene and **9** has prevented isolation of **9** to date. Addition of DME to the reaction mixture allowed for isolation of PhC≡Mo(OCMe(CF$_3$)$_2$)$_3$(DME) in low yield (20%). Similarly, treatment of **1** with 10 equiv of the unsymmetrical alkyne 4-biphenyl-1-butyne resulted in the formation of ArC≡Mo(OCMe(CF$_3$)$_2$)$_3$(NCAr) (**10**) (Ar = *p*-PhC$_6$H$_4$) (78%). Although bis(4-biphenyl)acetylene can be readily separated from **10**, separation from the remaining unsymmetrical alkyne has not been achieved to date.

Since the RC≡Mo(OC(CF$_3$)$_3$)$_3$ complexes were usually unstable upon attempts to isolate them as solids, stable benzylidyne analogs were sought. As shown in Scheme 5, direct conversion of **2** to ArC≡Mo(OR)$_3$(NCAr) was achieved via metathesis with bis(4-methoxyphenyl)acetylene (80%) or bis(4-biphenyl)acetylene (88%). Slow metathesis was observed with bis(4-biphenyl)acetylene due to the poor solubility of this alkyne under the reaction conditions. The increased Lewis acidity of **2** relative to **1** likely accounts for the direct scission of ArC≡CAr by **2**, a reaction that is not observed with **1.**

3.3. Nitride-to-alkylidyne complex conversions assisted by Lewis acids

Investigations of the influence of Lewis acids on metathesis initially focused on the effect that 2 equiv of magnesium bromide had on the alkyne metathesis activity of **5** and **6** with 20 equiv of Ph–C≡C–R (R = Et, Me) in three different solvents, $CDCl_3$, CD_2Cl_2, and C_6D_6 (Table 1). Magnesium bromide was selected for the studies because it promoted minimal catalyst decomposition under the reaction conditions, unlike some other Lewis acids (see Supporting Information). All reactions were monitored via ^{1}H NMR spectroscopy to within 5% equilibrium with their reaction quotients (*Q*) being reported in Table 3. An equilibrium amount of alkyne metathesis products corresponds to a K_{eq} = 0.25 with the aryl-containing products consisting of 33% unsymmetrical alkyne and 66% symmetrical alkyne. Since no evidence of polymer formation was observed this value is calculated assuming the absence of 3-hexyne (2-butyne) polymerization, as highlighted in Fig. 4. The corresponding solvent studies for **1** and **2** in the absence of a Lewis acid are also reported in Table 3.

Table 3
Solvent effect on metathesis of PhC≡CR catalyzed by nitride complexes.[a]

Catalyst	C_6D_6 (h)	CD_2Cl_2 (h)	$CDCl_3$ (h)	R	Temp (°C)	*Q*
5/$MgBr_2$	14[b]	4	11	Et	60	0.20 ± 0.01[c]
6/$MgBr_2$	43[d]	NR[e]	43[f]	Me	60	–
1	4	6	8	Me	RT[g]	0.25 ± 0.01[h]
2	9	13	7	Me	RT	0.24 ± 0.02[h]

[a] NMR scale reactions with 5 mol% catalyst.
[b] Toluene-d_8.
[c] 31% Diphenylacetylene/69% 1-phenyl-1-butyne.
[d] 15% Diphenylacetylene/85% 1-phenyl-1-propyne (*Q* = 0.03).
[e] NR = no reaction.
[f] 24% Diphenylacetylene/76% 1-phenyl-1-propyne (*Q* = 0.11).
[g] RT = room temperature.
[h] 33% Diphenylacetylene/67% 1-phenyl-1-propyne.

3.3.1. Solvent studies

In the absence of Lewis acids, the optimal solvents for alkyne metathesis activity with **1** and **2** were C_6D_6 and $CDCl_3$, respectively. Despite the increased Lewis acidity of **2** relative to **1**, more rapid alkyne metathesis activity was observed with **1** than with **2**. We attribute this difference to the presence of a coordinating ligand in **2** hindering access to the active catalyst. Schrock demonstrated a similar rate disparity in comparing Me$_3$CC≡Mo(OC(CF$_3$)$_2$Me)$_3$(DME) and Me$_3$CC≡Mo(OC(CF$_3$)$_3$)$_3$(DME). More rapid alkyne metathesis was observed with the former catalyst due to the presence of a less strongly bound DME ligand [29] In order to avoid overlapping resonances in the ^{1}H NMR spectrum during the solvent studies with **5**, 1-phenyl-1-butyne was employed in place of 1-phenyl-1-propyne. The preferred reaction medium with **5** was CD_2Cl_2 due to the increased solubility of magnesium bromide under the reaction conditions. Catalyst **6** displayed the highest conversion to diphenylacetylene in $CDCl_3$ prior to catalyst decomposition at 60 °C. The rate of metathesis can be enhanced relative to the rate of catalyst decomposition with **6** by increasing the reaction temperature to 80 °C, achieving an equilibrium mixture of alkyne metathesis products.

3.3.2. Nitride-to-alkylidyne moiety conversions with **6** assisted by Lewis acids

The presence of alkyne metathesis activity with **6** was surprising, since the conversion to an alkylidyne complex is least favorable thermodynamically and kinetically with **6** relative to the other nitride complexes investigated. The activity of **6** with 2 equiv of several different Lewis acids and 20 equiv of 1-phenyl-1-propyne was examined in $CDCl_3$ at 80 °C. The reactions were monitored to 20% diphenylacetylene and 80% 1-phenyl-1-propyne (*Q* = 0.07) (Table 4). Although seven different Lewis acids assisted in alkyne metathesis with **6**, only magnesium bromide resulted in further

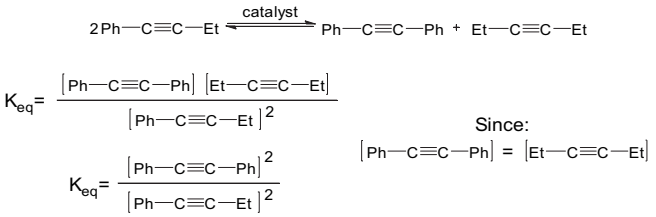


Fig. 4. Equilibrium calculations.

Table 4
Alkyne metathesis studies with 1-phenyl-1-propyne assisted by Lewis acids with complexes **5**, **6**, **1** and **2**[a]: Time to reported *Q*-value.

Entry	Lewis acid	Time (h)			
		5[b]	6[c]	1[d]	2[e]
1	$MgBr_2$	93	23[f]	NRE[g]	NRE
2	MgI_2	59	19	NRE	NRE
3	$TiCl(O^iPr)_3$	Dec[h]	88	Dec	Dec
4	$ZrCl_4$	Dec	11	6	NRE
5	$CuCl_2$	99	27	NRE	NRE
6	$CuBr_2$	59	27	NRE	NRE
7	BPh_3	NR[i]	Polymer[j]	NRE	5
8	HCl	Dec	NR	6	NRE
9	None	NR	NR	8	9
Q		0.06 ± 0.01	0.07 ± 0.01	0.20 ± 0.01	0.20 ± 0.01

[a] NMR scale reactions with 5 mol% catalyst.
[b] CD_2Cl_2 at 40 °C.
[c] C_6D_6 at 80 °C.
[d] $CDCl_3$ at room temperature.
[e] C_6D_6 at room temperature.
[f] $Q = 0.21$.
[g] NRE = no rate enhancement.
[h] Dec. = catalyst decomposition.
[i] NR = no reaction.
[j] Poly(3-hexyne) present.

conversion ($Q = 0.21$) to alkyne metathesis products upon additional heating. Some alkyne metathesis was observed in the presence of triphenylborane; however, unlike with the other Lewis acids, alkyne polymerization dominated as indicated by the formation of an insoluble gelatinous material. Additional Lewis acids were tested with no alkyne metathesis activity being observed (See supplementary information). There is presently no obvious trend in the Lewis acids that assist in alkyne metathesis with **6**. The length of time required to convert **6** to trace amounts of alkylidyne complex in order for alkyne metathesis to occur varied with each Lewis acid.

3.3.3. Nitride-to-alkylidyne moiety conversions with **5** assisted by Lewis acids

Examination of the activity of **5** with 20 equiv of 1-phenyl-1-propyne under its optimized reaction conditions (CD_2Cl_2, 40 °C) revealed that a subset of the Lewis acids that assisted the alkyne metathesis activity of **6** also did so with **5** (Table 4). The reactions were monitored to a composition of 20% diphenylacetylene and 80% 1-phenyl-1-propyne. No further alkyne metathesis was observed upon additional heating. As observed with **5**, an induction period was required for catalyst conversion prior to alkyne metathesis occurring. Additionally, no alkylidyne complexes were observed spectroscopically.

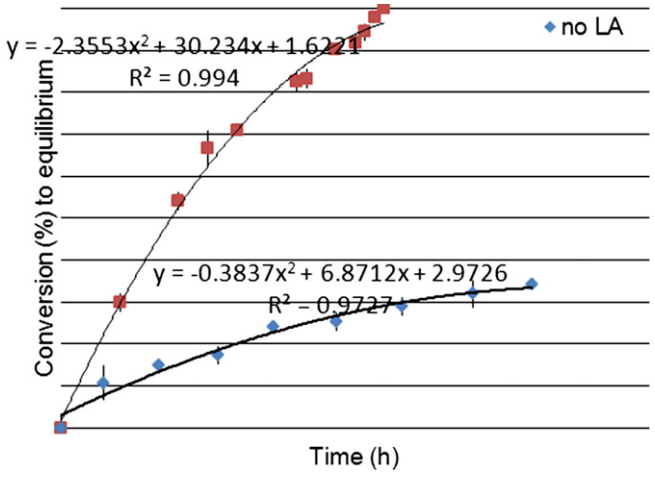


Fig. 5. Conversion toward equilibrium: alkyne metathesis of 1-phenyl-1-propyne with **2** and BPh_3.

Table 5
Alkyne effect on metathesis rate with **5** and Ph–C≡C–R (R = Et, Me) assisted by Lewis acids.[a]

Lewis Acid	Et (Time, h)	Me (Time, h)
$MgBr_2$	18	93
MgI_2	5.5	59
$CuCl_2$	44	99
$CuBr_2$	8[b]	59[b]
BPh_3	45 (polymer)	NR
None	NR[c]	NR
Q	0.22 ± 0.3[d]	0.07[b]

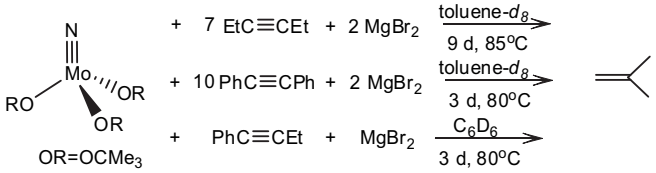
[a] NMR scale reactions with 5 mol% **5**, 40 °C, CD_2Cl_2.
[b] 20% Diphenylacetylene/80% 1-phenyl-1-propyne ($Q = 0.07 \pm 0.02$).
[c] NR = no reaction.
[d] 33% Diphenylacetylene/67% 1-phenyl-1-butyne.

3.3.4. Enhancing the rate of alkyne metathesis with **1** and **2** through Lewis acid assistance

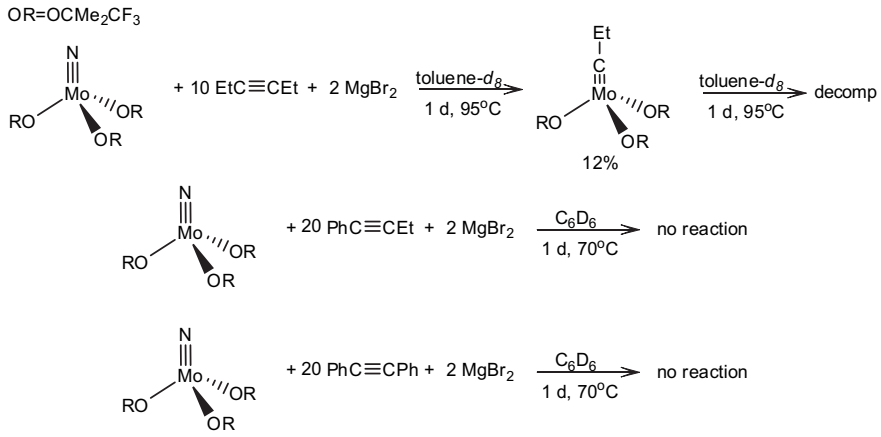
Activity studies were completed with **1** and **2** in the presence of 2 equiv of Lewis acid and 20 equiv of 1-phenyl-1-propyne to determine whether the rate of alkyne metathesis could be enhanced with these pre-catalysts (Table 4). These reactions were monitored to a composition of 31% diphenylacetylene and 69% 1-phenyl-1-propyne. With each catalyst, the solvent that resulted in the slowest rate of metathesis in the absence of a Lewis acid was employed in order to observe the greatest impact on metathesis rate. As observed with **5** and **6**, **1** required an activation period prior to observing alkyne metathesis under the reaction conditions ($CDCl_3$, room temperature). Only zirconium (IV) chloride and hydrochloric acid were found to enhance the rate of alkyne metathesis with **1**. Unlike **1**, triphenylborane was the only Lewis acid that assisted in the rate of alkyne metathesis with **2** in C_6D_6 at room temperature. No evidence of poly-3-heyxne formation was noted. In this case, the lack of an extended catalyst induction period is indicated in Fig. 5, with the rate of metathesis slowing as equilibrium is approached.

3.3.5. Substrate influence on alkyne metathesis assisted by Lewis acids with **5**

In addition to Lewis acids influencing the rate of alkyne metathesis, an unanticipated substrate-dependent rate difference was observed when comparing Ph–C≡C–Me and Ph–C≡C–Et with **5**. The rates of alkyne metathesis when R = Et were enhanced relative to those when R = Me (Table 5). Additionally, an equilibrium mixture of alkyne products was achieved when R = Et under the reaction conditions, since alkyne metathesis occurred at a more rapid rate than catalyst decomposition. The difference in alkyne metathesis rates might be attributed to a difference in 3-hexyne and 2-butyne polymerization rates; however, metathesis with



Scheme 6. Isobutylene formation with **6**.



Scheme 7. Attempted formation of alkylidyne complexes from **5**.

1-phenyl-1-propyne should then proceed faster than with 1-phenyl-1-butyne. The decreased rate of alkyne polymerization relative to alkyne metathesis as the substrate alkyl-chain (R group) length increases has been noted previously in alkyne metathesis systems [30]. Furthermore, no evidence of polymer formation was noted in the current study. The origin of the rate differences associated with alkyl-chain length upon catalysis with **5** and a Lewis acid is still under investigation.

*3.3.6. Attempted isolation of alkylidyne complexes from **5** to **6***

Now that the ability to form an alkylidyne complex from **5** and **6** in the presence of a Lewis acid had been established, isolation of an alkylidyne complex from the reaction mixture was desired. Since magnesium bromide was found to readily assist in alkyne metathesis, several attempts at isolating alkylidyne complexes were completed with this Lewis acid. Symmetrical alkyl and aryl-based alkynes and unsymmetrical alkynes were examined at elevated temperatures in aromatic solvents with both **5** and **6**. As shown in Scheme 6, the C—O bond scission product, isobutylene, was the only readily identifiable product in the reaction mixtures with **6**.

Unlike **6**, for **5** ^{1}H and ^{19}F NMR spectroscopies provided direct evidence of alkylidyne complex formation (12%) upon heating with 10 equiv of 3-hexyne and 2 equiv of magnesium bromide at 95 °C for 1 day (Scheme 7). Attempts to drive the formation of the propylidyne complex only resulted in destruction of the alkylidyne complex, which decomposes upon prolonged heating in the presence of magnesium bromide. Formation of alkylidyne complexes via treatment of **5** with other alkyne substrates was unsuccessful.

4. Conclusions

Although **5** and **6** could not serve as precursors to isolated alkylidyne complexes, the ability to use them as *in situ* pre-catalysts for alkyne metathesis in the presence of Lewis acids has been demonstrated. A comparison of the common alkyne metathesis pre-catalysts and catalysts as discussed by Moore and coworkers [31], reveals that the molybdenum nitride complexes can be synthesized in the fewest number of steps from commercially available sources with the exception of Mortreux's $Mo(CO)_6$/phenol system. Depending on the nitride precatalyst, alkyne metathesis can operate at room temperature to 80 °C, which is similar to the most commonly used catalyst for alkyne metathesis, $Me_3CC{\equiv}\oplus W(OCMe_3)_3$ [31]. Furthermore, we have demonstrated that the introduction of an appropriate Lewis acid to **1** or **2** can strongly enhance the rate of alkyne metathesis with **1** and **2**. The alkylidyne or benzylidyne analogs of **1** or **2** can be readily accessed via metathesis if they are desired. Future studies with these systems will focus on determining the mode of interaction of the Lewis acid with the nitride complexes. Additionally, the influence of Lewis acids on metathesis reactions with tungsten nitride complexes will be pursued.

Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. CHE-0449459. We also thank the University of Michigan for financial support.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.08.001.

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