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Highly Active Molybdenum−Alkylidyne Catalysts for Alkyne Metathesis: Synthesis from the Nitrides by Metathesis with Alkynes

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Olefin metathesis has had an enormous impact on synthetic chemistry over the past two decades, due to great improvements in catalyst design.[1−6] Although highly active homogeneous catalysts for the analogous alkyne metathesis reaction have been known for just as long, the latter process has seen less use until recently.[7−15] Widespread application of alkyne metathesis in the areas of small molecule, natural product, and polymer synthesis has apparently been frustrated either by the inconvenience of syntheses of highly active catalysts[8] or by the incompatibility of sensitive substrates with the somewhat harsher conditions required for the use of simpler "in situ" catalysts.[14,16] Very recently, several groups have reported the formation of highly active catalysts derived from Mo(N[*t*-Bu]-Ar)$_3$ (**1**)[8,10−13,17−20] and its analogue Mo(H)(η^2-Me$_2$CNAr)(N[*i*-Pr]-Ar)$_2$ (**2**).[21−23] Depending on the ancillary ligand set, catalysts derived from **1** and **2** display good functional group tolerance. Nevertheless, the intermediate complexes **1** and **2** are synthetically challenging; both are highly reactive air- and water-sensitive species capable of reductively cleaving N_2.[17,21] We report herein the formation of the exceptionally active alkyne metathesis catalyst EtC≡Mo(OC(CF$_3$)$_2$-Me)$_3$(DME) (**3**-DME; DME = 1,2-dimethoxyethane) in high yield from N≡Mo(OC(CF$_3$)$_2$Me)$_3$ (**4**) or N≡Mo(OC(CF$_3$)$_2$Me)$_3$(NCMe) (**4**-NCMe) upon reaction with 3-hexyne at elevated temperature. Complex **3**-DME was first prepared two decades ago by Schrock, who demonstrated its activity in alkyne metathesis reactions and investigated its mechanism.[24] Treatment of N≡Mo(OC(CF$_3$)$_3$)$_3$-(NCMe) (**5**-NCMe) with 3-hexyne and DME under similar conditions likewise yields another highly active metathesis catalyst, EtC≡Mo(OC(CF$_3$)$_3$)$_3$(DME) (**6**-DME). As the synthesis of **4**, **4**-NCMe, and **5**-NCMe is simple and straightforward, reaction of these compounds with 3-hexyne is an exceptionally facile route to multigram quantities of extremely active Mo-based alkyne metathesis catalysts.

As part of a study of the reactivity and relative stability of nitride and alkylidyne complexes of the *d*-block elements, we recently reported the synthesis of the terminal nitrido species **4** and **5**-NCCH$_3$ and degenerate N-atom exchange processes with and among nitriles mediated by these complexes.[25] A related tungsten complex, N≡W(O-*t*-Bu)$_3$ (**7**), is known to catalyze the same process; DFT calculations support an azametallacyclobutadiene intermediate.[26]

Having established that the nitrido moiety in **4**-NCMe and **5**-NCMe is active in degenerate N-atom exchange with nitriles, we next investigated reactions of these complexes with alkynes. Among related tungsten compounds, N≡W(OAr)$_3$ (**8**; Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) is formed rapidly and quantitatively when *t*-BuC≡W(OAr)$_3$ (**9**) is treated with a nitrile, such as MeCN;[27] similarly, PhC≡W(OC(CF$_3$)Me$_2$)$_3$ (**10**) and PhC≡W(OSi-*t*-BuMe$_2$)$_3$ (**11**) react with aryl nitriles to afford N≡W(OC(CF$_3$)Me$_2$)$_3$ (**12**) and N≡W(OSi-*t*-BuMe$_2$)$_3$ (**13**), respectively.[28,29] These results indicate a strong preference for nitride rather than alkylidyne ligation at this metal center. However, periodic trends predict an eventual crossover in the relative stability of alkylidyne and nitrido complexes as the metal center becomes more electronegative.[30]

At room temperature, we do not observe alkylidyne formation from compounds **4**, **4**-NCMe, or **5**-NCMe upon reaction with nitriles or symmetrical alkynes. However, when solutions of **4**, **4**-NCMe, and **5**-NCMe are exposed to unsymmetrical alkynes, products of alkyne metathesis appear, albeit rather slowly. For example, at 92 °C, 10 mol % of **4** yielded 58% conversion to PhC≡CPh in 19 h; when **5**-NCMe was used under the same conditions, conversion to PhC≡CPh was complete within this time period. Equilibrium was not established in these reactions due to consumption of coproduced MeC≡CMe, which was polymerized under these conditions. Polymerization of MeC≡CMe is often seen with alkylidyne complexes, such as **3**-DME, for example.[24] At 80 °C, mixtures initially composed of equimolar 3-hexyne and 4-octyne approached equilibrium with 3-heptyne to the extent of 71 and 92% after 3 h with 5 mol % of **4** and **5**-NCMe, respectively. Equilibrium was reached soon thereafter. The reactions proceeded similarly rapidly in CD_2Cl_2. Likewise, EtC≡CMe gave rise to EtC≡CEt and MeC≡CMe slightly more rapidly (again, MeC≡CMe was ultimately consumed). However, in THF, we observed no metathesis whatsoever of PhC≡CMe or EtC≡CMe. DME similarly inhibits metathesis. In C_6D_6 with 3 equiv added DME, metathesis occurred very slowly, with the first products being observed after 3 days with **4** and after 24 h with **5**-NCMe (6.7 mol % catalyst).

Although no alkylidyne complex is observed by NMR spectroscopy under these conditions, these results suggest the possibility that an alkylidyne complex is being formed from the nitrido complex to a small extent. However, two initial observations rule out reversible formation of alkylidyne complex in an equilibrium that favors the nitrido complex. Unlike **9** and **10**, EtC≡Mo(OC-(CF$_3$)$_2$Me)$_3$ (**3**),[24] **3**-DME, and **6**-DME fail to react with nitriles, except to coordinate them reversibly. No terminal nitrido complexes are formed in these cases. Furthermore, experiments involving treatment of **4** and **5**-NCMe with a mixture of excess alkyne (R−C≡C−R) and excess nitrile (R′−C≡N) reveal no crossover of the organic radicals (R, R′); use of unsymmetrical alkyne shows that alkyne metathesis occurs, but without incorporation of the R′ group from the nitrile.

Heating of solutions of **4**, **4**-NCMe, and **5**-NCMe with 3-hexyne and 1 equiv of DME to 95 °C in benzene results in complete conversion to the corresponding propylidyne complexes over several days. Thus, the alkylidyne complexes are formed *irreversibly* from the nitrido complexes, but with a large activation barrier. However, DME is not required for this conversion but in fact inhibits the reaction. When DME is not present in the initial mixture, conversion to the propylidyne complex **3** is quantitative after only 14.5 h at 95 °C. DME is added to the solution in order to facilitate isolation of the alkylidyne complexes in the form of the more crystalline DME adducts **3**-DME and **6**-DME. Both preparations afford **3**-DME in approximately 60% yields on a multigram scale.

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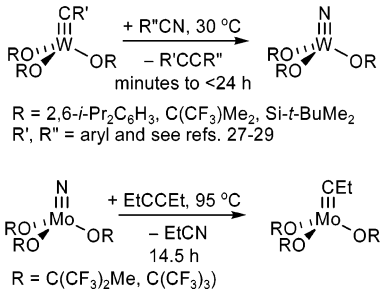
Scheme 1 . Reversal of Nitride versus Alkylidyne Ligand Preference in W versus Mo Complexes



The reversal of nitride versus alkylidyne ligand preference for these new Mo complexes compared to their W analogues in systems containing both nitrile and alkyne is depicted in Scheme 1.

Alkylidyne synthesis was also performed in situ by preincubating **4** with 3-hexyne and 1 equiv of DME in C_6D_6 at 95 °C for 13 h. Subsequent addition of 20 equiv of 1-phenyl-1-propyne demonstrated dramatically faster alkyne metathesis than in the nonincubated system discussed previously, proceeding to 48.5% completion after only 2 h at room temperature. However, as the alkylidyne complex is the active catalyst, we find it most convenient to use isolated **3**-DME in order to effect alkyne metathesis under the mildest conditions and in the shortest time.

In summary, we have found that use of more highly fluorinated alkoxide ligands, coupled with a change in the metal from tungsten to molybdenum, results in reversal of the previously observed thermodynamic preference for nitride as opposed to alkylidyne ligation in trisalkoxide complexes of the group 6 metals. Thus, we have discovered a very facile synthesis of some highly active alkyne metathesis catalysts. This synthesis is likely to be quite general for molybdenum−alkylidyne complexes that bear alkoxide or aryloxide ligands substituted with electron-withdrawing groups; we are currently pursuing this idea both in order to identify complexes with superior activity and functional group tolerance and in order to identify the crossover point for favoring alkylidyne over nitride ligation in complexes of Mo and W.

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Supporting Information Available: Characterization data for new compounds, synthetic data for new compounds and old compounds made by new routes, and conditions for the reactions of **3**−**6** with substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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