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A reductive recycle strategy for the facile synthesis of molybdenum(VI) alkylidyne catalysts for alkyne metathesis†

Wei Zhang, Stefan Kraft and Jeffrey S. Moore*

Roger Adams Laboratory, Departments of Chemistry, Materials Science & Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA. E-mail: js-moore@uiuc.edu; Fax: 1-217-244-8068; Tel: 1-217-244-4024

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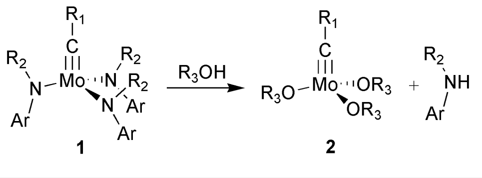
A convenient synthesis of trisamido molybdenum(VI) alkylidyne complexes has been developed, in which the key step is the addition of a geminal dichloride to a trisamido molybdenum(III) complex in the presence of magnesium to continuously recycle unwanted side product 4, selectively generating the desired alkylidyne complexes in high yield.

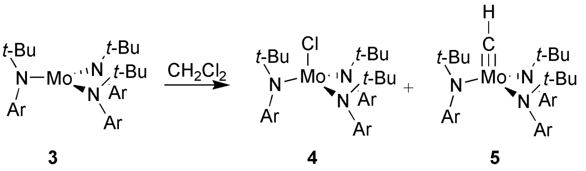
Despite the tremendous impact of alkene metathesis on organic and polymer synthesis over the last decade,[1] the analogous alkyne metathesis chemistry is a less developed synthetic method. The alkyne metathesis catalysts that have been most widely used for natural product synthesis and the preparation of phenylene ethynylene polymers are based on molybdenum or tungsten complexes.[2] Unfortunately, the most readily available of these catalysts are a mixture of catalytic and non-catalytic species that require high temperatures for metathesis activity with limited functional group tolerance. In this communication we outline a convenient synthesis of trisamido molybdenum(VI) alkylidyne complexes and their conversion into highly active alkyne metathesis catalysts.

The first homogeneous catalytic alkyne metathesis dates back more than 25 years when Mortreux and Blanchard discovered that $Mo(CO)_6$ and various phenols metathesize diphenylacetylenes at 160 °C.[3] The active form of this catalyst remains unknown, and in spite of high temperature and limited functional group tolerance, Mori[3b] and Bunz[2d] have used the reaction extensively for both small molecule and polymer synthesis. The first well-defined alkyne metathesis catalyst was the tungsten alkylidyne complex $(t\text{-BuO})_3WC(t\text{-Bu})$ developed by Schrock in the early 1980's.[4] This catalyst can metathesize alkynes under milder conditions (25–60 °C), but thio ethers, amines or crown ether segments are not tolerated. Schrock, and more recently Cummins, have reported that analogous trialkoxymolybdenum(VI) carbyne complexes $(R_3O)_3MoCR_1$(**2**) are highly active alkyne metathesis catalysts even at room temperature,[5] but their scope has not been reported in detail. Although trialkoxy alkylidyne **2** can be conveniently obtained from alcoholysis of the metathesis inactive triamide **1** (eqn. 1), the tedious and multistep nature of the synthesis of starting complex **1**[5,6] presents a practical limitation to this potentially useful catalyst. A related alkyne metathesis catalyst was developed by Fürstner who combined readily available[7] $Mo[N(t\text{-Bu})Ar]_3$ (Ar = 3,5-$C_6H_3Me_2$) (**3**) with dichloromethane to produce a mixture of $ClMo[N(t\text{-Bu})Ar]_3$ (**4**) and $HCMo[N(t\text{-Bu})Ar]_3$ (**5**) (eqn. 2). This mixture provided alkyne metathesis activity at 80 °C with good functional group compatibility.[8,9] The catalytically active species is derived from monochloride **4** whereas methylidyne **5** is almost metathesis inactive.[10]



(1)

Given that Fürstner's method directly produces alkylidyne **5**, which is the precursor to Cummins' active trialkoxyalkylidyne **2**, an expedient synthesis of complex **2** could involve redirecting the reaction in eqn. 2 to favor production of $HCMo(N[t\text{-Bu}]Ar)_3$. We anticipated that a reducing agent could selectively react with monochloride **4** returning it to starting complex **3**, while leaving complex **5** unaffected. In the presence of excess methylene chloride, the net result would be a reductive recycle approach to selectively generate the desired complex **5** in one pot (eqn. 3). This concept was demonstrated by the following experiment. When a 0.1 M solution of triamide **3** was treated with $^{13}CH_2Cl_2$ (10 fold excess) in THF-d_8 (ferrocene as internal standard), a 2 : 1 mixture of monochloride **4** and methylidyne **5**-^{13}C was obtained in 97% yield by ^1H NMR integration of the *t*-Bu peaks at 24.41 ppm and 1.46 ppm. Addition of 54 mg magnesium (2.2 mmol) followed by stirring for 45 min at room temperature, resulted in the clean formation of methylidyne **5**-^{13}C (> 90% yield) as evidenced by ^1H and ^{13}C NMR. Neither the starting triamide **3** nor monochloride **4** could be detected. A small amount of *N-tert*-butyl aniline from hydrolysis was the only detectable side product.



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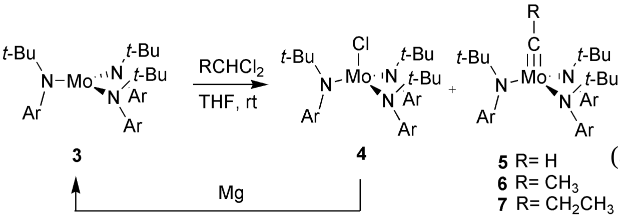

(3)

Given the feasibility of the reductive recycle approach, a preparatively useful procedure was developed. Several reducing agents and solvent combinations were examined but none of them were as successful as magnesium in THF. Zinc–copper couple, manganese and samarium slowly produced **5** at 50 °C, but additional unknown products formed under these conditions. At 70 °C, monochloride **4** decomposes quickly which makes the reductive recycle strategy not feasible at elevated temperature. The superior reductive efficiency exhibited by magnesium prompted us to select this reducing agent for further exploration.

We next examined the scope of the reaction with various geminal dihalides. The reaction was not successful when attempted with benzal chlorides. In contrast, 1,1-dichloroethane (15 equiv.) reacted with molybdenum triamide **3** to generate ethylidyne **6** (eqn. 3) in very good yield. When triamide **3** was treated with 1,1-dichloropropane (15 equiv.) in the presence of magnesium, a large quantity of a side product, presumably derived from a Grignard reaction, unexpectedly formed instead of desired product. This byproduct was eliminated by lowering the quantity of 1,1-dichloropropane to two-fold relative to

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† Electronic supplementary information (ESI) available: spectral data. See http://www.rsc.org/suppdata/cc/b2/b212405j/

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molybdenum triamide **3**. Under these conditions, the desired propylidyne **7** was obtained cleanly and in high yield.[11] The X-ray crystal structure[12] of propylidyne **7** (Fig. 1) revealed a characteristic Mo–C triple bond distance of 1.735(2) Å,[5] in accord with the observed ^{13}C NMR chemical shift of 302.6 ppm for the carbyne carbon (C37). The X-ray analysis of **7** also showed the close packing of the amido ligands on one side of this molecule. The aryl rings adopt approximately three-fold symmetry. Thereby a pocket is formed around the Mo center which shields the central metal quite efficiently.

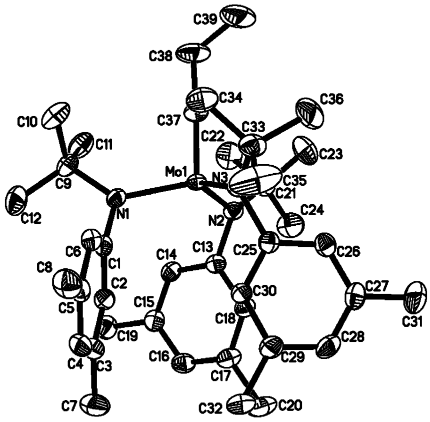
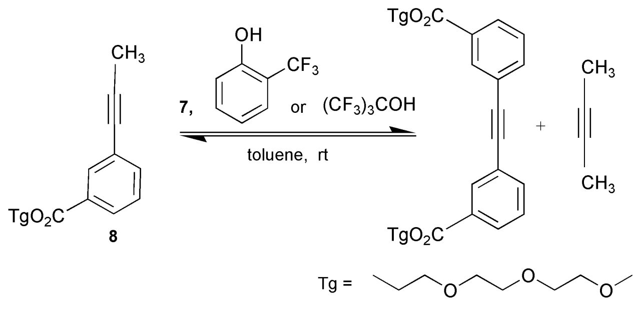


Fig. 1 X-Ray crystal structure of complex **7**. Anisotropic displacements are drawn at 50% probability, hydrogen atoms are omitted for clarity. Selected bond lengths in Å and bond angles in °. Mo–N (aver.) 1.981(3), Mo–C37 1.735(2), C38–C37–Mo 177.4(3), C37–Mo–N 102.51(11).

Given that a preparatively useful synthesis of trisamido molybdenum alkylidynes was in hand, we next wanted to demonstrate that these complexes are useful precursors for alkyne metathesis. Alcoholysis of 15 mg molybdenum(VI) propylidyne complex **7** (22 µmol) with 3 equiv. of α,α,α-trifluoro-*o*-cresol or perfluoro-*tert*-butyl alcohol in toluene generated a trialkoxymolbdenum(VI) propylidyne complex that was used directly for metathesis studies. When 28 mg of benzoate ester **8** (90 µmol) was added to this catalyst solution, the equilibrium ratio of 4:1 was reached in 22 h at room temperature.

In summary, we developed a practically useful method to synthesize trisamido molybdenum(VI) alkylidyne complexes based on a reductive recycle approach. This method provides a convenient, large-scale preparation of trisamido molybdenum(VI) alkylidyne complexes in pure form. Alcoholysis of molybdenum(VI) propylidyne **7** with α,α,α-trifluoro-*o*-cresol or perfluoro-*tert*-butyl alcohol provide active catalysts for alkyne metathesis at room temperature. The scope of this reductive recycle strategy is still under investigation to evaluate its feasibly toward the synthesis and isolation of trialkoxymolybdenum(VI) alkylidyne catalysts for alkyne metathesis.



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10 Carbyne complex **5** is inert to metathesis as demonstrated by Fürstner using stoichiometry studies on the mixture of **4** and **5**. Using pure **5** we have followed up on this experiment and conclude that **5** is *catalytically*, inactive. Also see: ref 4: R. R. Schrock, D. N. Clark, J. Sancho, J. H. Wengrovius, S. M. Rocklage and S. F. Pedersen, *Organometallics*, 1982, **1**, 1645; R. R. Schrock, *Polyhedron*, 1995, **14**, 3177.

11 Preparation of molybdenum(VI) propylidyne **7**: all manipulations were performed in an inert argon atmosphere. To a solution of molybdenum triamide **3** (0.5053 g, 0.81 mmol) in THF (18 mL) was added $CH_3CH_2CHCl_2$ (160 µL, 1.6 mmol) resulting in a color change from red to dark amber. Magnesium turnings (0.2412 g, 10.1 mmol) were added and the resulting mixture was stirred for 1.5 h at room temperature. The solvent was removed *in vacuo*, and the residue was redissolved in pentane (25 mL). The solid precipitate was removed by filtration and the filtrate was concentrated *in vacuo*. The product was obtained as a light yellow powder in 91% yield (492 mg). ^{1}H NMR (d_8-THF, 500 MHz, −80 °C): δ 6.72 (3H, s), 5.73 (6H, s), 3.53 (2H, q, *J*, = 7.5Hz), 2.09 (18H, s), 1.46 (3H, t, *J*, = 8.0Hz), 1.27 (27H, s); ^{13}C NMR (d_8-THF, 125 MHz): δ 302.6, 151.4, 137.5, 131.0, 128.0, 61.3, 45.7, 34.0, 21.7, 14.8 (coalesce of different isomers was observed when temperature gradually raised from −80 °C to room temperature); MS (EI): *m*/*z* (%): M^+ 665.4 (13), 610.3 (15), 552.2 (8), 490.2 (7), 162.1 (100), 121.1 (40); HR-MS (EI) ($C_{39}H_{59}MoN_3$): calcd 665.3607, found 665.3605; elemental analysis cald (%) for $C_{39}H_{59}MoN_3$ (665.83): C 70.35, H 8.93, N 6.31; found C 69.75, H 8.84, N 6.25%.

12 *Crystal data*, for **7**: Suitable single crystals for the X-ray diffraction study were grown from *n*-pentane. $C_{39}H_{59}MoN_3$, M = 665.83, monoclinic, space group $P2_1/c$, a = 19.144(10), b = 10.513(6), c = 19.324(11) Å, β = 104.075(9)°. V, = 3772(4) Å^3, Z, = 4, ρ_{calcd} = 1.172 g cm^{-3}; μ (Mo–Kα) = 0.376 mm^{-1}, T, = 193(2) K, 39471 reflections measured, 6919 unique (R_{int} = 0.0446) which were used in all calculations. The final $wR(F^2)$, was 0.0844 (all data). CCDC 200432. See http://www.rsc.org/suppdata/cc/b2/b212405j/ for crystallographic data in .cif or other electronic format.