Reduction of Molybdenum(V) Chloride with Various Reducing Metals: Reactivity Correlations with the Descendant Lewis Acids

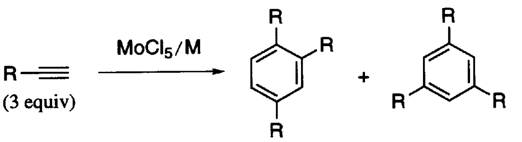
Ryuichiro Hara,* Qiaoxia Guo, and Tamotsu Takahashi*

Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University and CREST, Science and Technology Corporation (JST), Sapporo 060-0811

(Received October 26, 1999; CL-990913)

Reactivity of low-valent molybdenum prepared from $MoCl_5$ with various reducing metals in DME, was dependent on the reducing metals in the order of Al > Sn, In > Zn, Mg, Li in the case of cyclotrimerization of alkynes. This order is parallel to the acidity of the descendant Lewis acids.

Low-valent molybdenum species have attracted attention with their diverse coordination patterns.[1] Reduction of $MoCl_5$ (or more precisely described as a dimer, Mo_2Cl_{10}) with main group metals as the reducing agent seems to be the most convenient way to prepare the low-valent molybdenum species. During the course of our study on the reaction of low valent molybdenum compounds, we found novel correlation between reactivity of the molybdenum compounds and acidity of the descendant Lewis-acid of the reducing metals. We would like to report here that the reactivity of low-valent molybdenum compounds prepared from $MoCl_5$ with various reducing metals in DME.[2]



(1)

The comparison study of various reducing metals for the reduction of molybdenum pentachloride in the case of cyclotrimerization of 1-octyne (eq. 1) is shown in Table 1 (entry 1–6). The procedure is as follows; a mixture of $MoCl_5$ (1 mmol) and 5 mL of DME was treated with reducing metals (Al, Sn, In, 1 mmol; Zn, Mg, 1.5 mmol; Li, 3 mmol)[3] and heated at 50 °C for 3 h. To the reaction mixture was added 1-octyne (3 mmol) and then the mixture was stirred at 50 °C for 6 h. The reaction was quenched with 3M HCl *aq.* and organic products were extracted with Et_2O. The products were analyzed by GC.

In the cyclotrimerization of 1-octyne using the $MoCl_5$/Al combination, 1,2,4-tri-*n*-hexylbenzene (**1**) and 1,3,5-tri-*n*-hexylbenzene (**2**) were obtained in 90% combined yield in a ratio of 8:1 (entry 1). Moderate yields and selectivities were obtained when In or Sn was used for the reduction of $MoCl_5$ (entry 2,3). Unexpectedly, strong reducing metals such as Zn, Mg and Li (entry 4–6) gave poor yields and poor selectivities. This result indicates that the yields are roughly in the order of Al > Sn, In > Zn, Mg, Li. Interestingly, this result is closely parallel to the acidity of the descendant Lewis acids, $AlCl_3$ > $SnCl_4$ > $InCl_3$ > $ZnCl_2$ > $MgCl_2$ > LiCl.[4] This suggests that the metal-chloride moiety such as Al-Cl, Sn-Cl and In-Cl has a cooperative effect with the reduced molybdenum in the cyclotrimerization of alkynes.

Table 1. Cyclotrimerization of 1-octyne with $MoCl_5$/ reducing metals[a]

	Metal	Conditions	Yield/%[b]	Ratio of **1**:**2**[c]
1	Al	80 °C, 1 h	90	8:1
2	Sn	80 °C, 3 h	75	3.5:1
3	In	80 °C, 3 h	70	6:1
4	Zn	80 °C, 3 h	44	1.4:1
5	Mg	80 °C, 3 h	34	1.1:1
6	Li	80 °C, 24 h	32	3.3:1

[a]Reaction conditions: $MoCl_5$ (1 mmol) was treated with reducing metals. (Al, Sn, In (1 mmol), An, Mg (1.5 mmol), Li (3 mmol) in DME (5 mL), 80 °C, 1 h, then 1-octyne was added. [b]Combined yields were determined by GC. [c]Ratio was determined by ^{1}H-NMR.

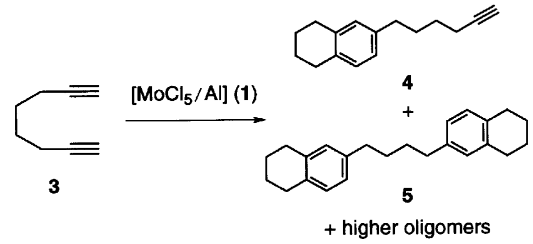
Table 2. Cyclotrimerization of RC≡CH (R = Ph, $SiMe_3$) with $MoCl_5$/Al, Sn, or In.[a]

	Alkyne	Metal	Conditions	Yield/%[b]	Ratio of **1**:**2**[c]
1	Ph—≡	Al	50 °C, 3 h	92	8:1
2		Sn	80 °C, 3 h	94	12:1
3		In	80 °C, 1 h	94	13:1
4	Me_3Si—≡	Al	50 °C, 24 h	40	1:9
5		Sn	50 °C, 24 h	51	1:3.5
6		In	50 °C, 24 h	54	1:2

[a]Reaction conditions: $MoCl_5$ (1 mmol) was treated with Al, Sn, or In (1 mmol) in DME (5 mL), 80 °C, 1 h, and then alkynes were added. [b]Combined yields were determined by GC. [c]Ratio was determined by ^{1}H-NMR.

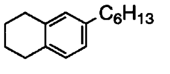
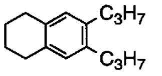
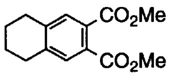
It is clear that Al, Sn and In are suitable reducing metals for $MoCl_5$ in trimerization of alkynes. Therefore, for other alkynes such as phenylacetylene and trimethylsilylacetylene, Al, Sn and In were used (Table 2). For phenylacetylene, Al, Sn and In gave comparable results (entry 1–3); however, In gave the best regioselectivity (13:1). For trimethylsilylacetylene, because of its sterically demanding substituent, 1,3,5-tris(trimethylsilyl)benzene was predominantly obtained (entry 4–6). The ratio varies from the case of Al (1:9) to that of In (1:2), again it differs from one metal to another.

In a reaction of 3 equiv of 1,7-octadiyne (**3**) with 1 equiv of $MoCl_5$ and 1 equiv of Al at 50 °C for 1 h, partially cyclized dimer **4** was obtained in 89% yield (eq. 2). A prolonged reac-



(2)

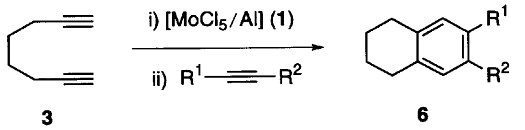
Table 3. Cross-cyclization of alkynes with 1,7-octadiyne[a]

Alkyne	Product		Yield/%[b]
$C_6H_{13}-\equiv$		**6a**	41
$C_3H_7-\equiv-C_3H_7$		**6b**	51
$MeO_2C-\equiv-CO_2Me$		**6c**	49

[a]Reaction conditions: $MoCl_5$ (1 mmol), Al (1 mmol), 1,7-octadiyne (1 mmol), DME (5 mL), 50 °C, 1 h; $R^1C{\equiv}CR^2$ (1 mmol), 50 °C, 1 h. [b]Yields were determined by GC.

tion time (6 h) at 80 °C afforded trimer **5** in 46% along with undefined higher oligomers.

Because the cyclotrimerization stage is more sterically demanding than the preceding dimerization, we expected cross-trimerization of α,ω-diyne and another molecule of alkyne. Therefore, 1,7-octadiyne (**3**) was treated at 50 °C for 1 h with a stoichiometric amount of $MoCl_5$/Al and an alkyne was added to the reaction mixture (eq. 3). The results are shown in Table 3. With 1-octyne, 2-*n*-hexyl-5,6,7,8-tetrahydronaphthalene (**6a**) was obtained in moderate yield of 41%. Small amounts of homo-coupling compounds were detected. It was striking that disubstituted alkynes could be used as the counterpart. Therefore, with 4-octyne and dimethyl acetylenedicarboxylate (DMAD), 2,3-di-*n*-propyl- and 2,3-bis(methoxycarbonyl) derivatives (**6b** and **6c**) were obtained in 51% and 49% yield, respectively. The yields are not yet satisfactory; however, this result suggests that the mechanism for the trimerization of alkynes by the $MoCl_5$/Al system is explained by a stepwise cyclization presumably involving molybdacyclopentadiene.[5]



(3)

3 **6**

We have, so far, no definite information on the structure of the $MoCl_5$/Al mixture; however, we assume an associative structure with μ-bridging chlorine atoms as shown in Figure. 1.

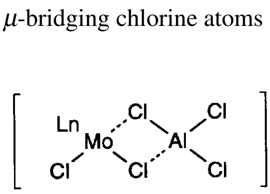


Figure. 1. Possible structure for the mixture of $MoCl_5$/Al.

This type of association between a low-valent Mo and an Al(III) halide is known in a few cases.[6] In addition, tetranuclear form $Mo_2Cl_4(AlCl_3)_2$ should be also considered as Cotton and co-workers reported in a related study.[7]

In summary, we found a relation between the reactivity of low-valent molybdenum and the reducing metals. Characterization of $MoCl_5$/metal composites and elucidation of the role of reducing metals in the trimerization reactions of alkynes must await further studies.

References and Notes

1 The group 6 metal complexes whose charges on the metal centers are from -2 to +6 are widely covered, see "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, E. W. Abel, Pergamon, Oxford (1982), Vol. 3, Chap. 27.1–27.2, pp. 1079–1253; "Comprehensive Organometallic Chemistry II," ed by E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon, Oxford (1995), Vol. 5, Chap. 3–8, pp. 155–549; "Comprehensive Coordination Chemistry," ed by G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon, Oxford (1987), Vol. 3, Chap. 36.1–36.6, pp. 1229–1444.

2 For general reviews on cyclotrimerization reactions, see N. E. Schore, "[2+2+2] Cycloadditions," in "Comprehensive Organic Synthesis," ed by B. M. Trost, I. Fleming, Pergamon, Oxford (1991), Vol. 5, pp. 1129; D. B. Grotjahn, "Transition Metal Alkyne Complexes: Transition Metal-catalyzed Cyclotrimerization" in "Comprehensive Organometallic Chemistry II," ed by E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon, Oxford (1995), Vol. 12, pp. 741.

3 Al, Sn, Zn: powder; In: small particles; Mg: turnings; Li: slices.

4 ^{1}H-NMR chemical shift differences (Dd) of crotonaldehyde on complexation with various Lewis acids were reexamined in order to evaluate the Lewis acidity of $AlCl_3$, $SnCl_4$, $InCl_3$ and $ZnCl_2$ by exactly following the procedures described in, R. F. Childs, D. L. Mulholland, and A. Nixon, *Can. J. Chem.*, **60**, 801 (1982). From the results given below, we may safely conclude that the order of Lewis acidity is $AlCl_3 > SnCl_4 > InCl_3 > ZnCl_2$. $\Delta\delta$ (CD_2Cl_2) (H_1, H_2, H_3, H_4 of crotonaldehyde, respectively): $AlCl_3$: -0.23, +0.77, +1.32, +0.45 (-0.20, +0.76, +1.23, +0.47, *lit.*); $SnCl_4$: +0.02, +0.49, +0.86, +0.28 (+0.02, +0.50, +0.87, +0.29, *lit.*); $InCl_3$: -0.02, +0.18, +0.37, +0.08; $ZnCl_2$: -0.02, +0.09, +0.13, +0.03.

5 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, **1978**, 221; S. Slater and E. L. Muetterties, *Inorg. Chem.*, **19**, 3337 (1980); S. Slater and E. L. Muetterties, *Inorg. Chem.*, **20**, 946 (1981); M. Green, P. A. Kale, and R. J. Mercer, *J. Chem. Soc., Chem. Commun.*, **1987**, 375; M. J. Chetcuti, L. A. DeLiberato, P. E. Fanwick, and B. E. Grant, *Inorg. Chem.*, **29**, 1295 (1990).

6 A. Greco, F. Pirinoli, and G. Dall'asta, *J. Organomet. Chem.*, **60**, 115 (1973); For $MoCl(\eta^3\text{-}C_3H_5)(\eta^6\text{-arene})(Cl_2AlEt)$, see; M. L. H. Green and J. Knight, *J. Chem. Soc., Dalton Trans.*, **1974**, 311; M. L. H. Green and J. Knight, *J. Chem. Soc., Dalton Trans.*, **1976**, 213.

7 F. A. Cotton, J. L. Hubbard, D. L. Lichtenberger, and I. Shim, *J. Am. Chem. Soc.*, **104**, 679 (1982); P. A. Agaskar, F. A. Cotton, D. R. Derringer, G. L. Powell, D. R. Root, and T. J. Smith, *Inorg. Chem.*, **24**, 2786 (1985); F. L. Campbell, III, F. A. Cotton, and G. L. Powell, *Inorg. Chem.*, **24**, 4384 (1985); P. A. Agaskar and F. A. Cotton, *Inorg. Chem.*, **25**, 15 (1986).