Silanol–molybdenum hexacarbonyl as a new efficient catalyst for metathesis of functionalised alkynes under microwave irradiation

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Abstract—The catalytic mixture based on $Mo(CO)_6$ was re-examined in the metathesis of 4-methoxytolan. Silanols (**4**) or (**5**) were found to be very active as co-catalysts. The metathesis of functional alkynes was convenient and rapidly achieved in octane as solvent under microwave irradiation in a resonance cavity. © 2001 Elsevier Science Ltd. All rights reserved.

The metathesis of alkynes has received less attention than that of alkenes because alkynes and active alkyne metathesis catalysts are less common than their alkene counterparts. Metathesis of alkenes generally results in a mixture of *Z* and *E* isomers and the stereochemistry cannot at present be properly controlled. However, alkynes are readily available and are precursors of stereospecific alkenes. Ring opening of strained cycloalkynes catalysed by well defined carbyne was first described by Schrock[1] using defined metallocarbenes. Recently these carbyne complexes have been used in ring formation of functional cycloalkynes;[2] however, these carbynes are not readily available and are air sensitive.

The first homogeneous catalyst (phenol+$Mo(CO)_6$) for alkyne metathesis was described by Mortreux[3] and we have described the use of such a catalyst [4-chlorophenol+$Mo(CO)_6$] in the metathesis of functional alkynes.[4] Although this catalyst has been use recently in metathesis of functional alkynes,[5] we decided to re-examine the potential of the metathesis of acyclic functional alkynes in order to find a more active and more convenient catalyst. Initially, we chose the cross-metathesis of methoxytolan as a model of funtionalised alkyne

metathesis (Scheme 1). An equilibrium was observed (**1**)/(**2**)/(**3**) = 2/1/1 when metathesis took place.

First we tried using 4-chlorophenol with a metal complex other than molybdenum hexacarbonyl. The substitution of $Mo(CO)_6$ by $[Rh(CO)_2Cl]_2$, $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$ or $W(CO)_6$ did not undergo metathesis. We studied the influence of temperature in the formation of the catalyst: the activity of $Mo(CO)_6$/chlorophenol began at 110°C, and the solution obtained after thermal activation did not catalyse the metathesis of methoxytolan at room temperature. Some form of thermal activation seems necessary for observing the metathesis of methoxytolan.

Next we explored the use of co-catalysts other than 4-chlorophenol. Under the same conditions, 4-trifluromethylphenol,[5] 2,4-dichlorophenol, 2,4,6-tribromophenol, 2,4-dimethylphenol are also active as co-catalysts. It is interesting to note that a hindered phenol like 2,4,6-tribromophenol is active because hindered phenols were used in designing selective and tolerant carbene catalysts in olefin metathesis. In all cases the equilibrium was obtained with a ratio of alkyne/Mo/phenol = 20/1/20. It is possible to diminish
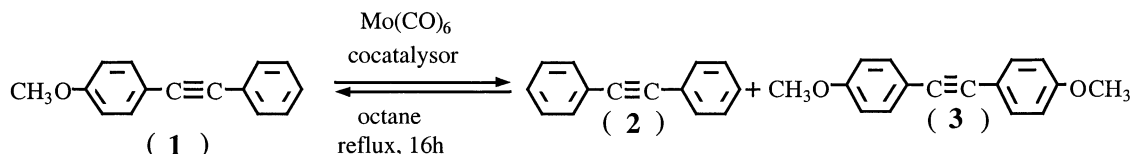
Scheme 1. Metathesis of 4-methoxytolan.

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the alkyne/phenol ratio and determine the activity. We found that the activity of the catalyst increased when the acidity of phenol was increased: 2,4,6-tribromophenol (pK_a 6.2)–2,4-dichlorophenol (pK_a 7.7)>4-trifluromethylphenol ($pK_a=8.67$)>4-chlorophenol ($pK_a=9.4$)>phenol ($pK_a=9.9$)–2,4-dimethylphenol ($pK_a=10.6$).

Dimolydenum tetraacetate ($Mo_2(OAc)_4$) in presence of 4-chlorophenol catalyses the metathesis of 4-methoxy-tolan. Dimolybdenum tetraacetate is formed by the reaction of acetic acid on molybdenum hexacarbonyl; however, we did not observe metathesis of 4-methoxytolan in acetic acid in the presence of $Mo(CO)_6$ when heated. We think that a complex with a molybdenum–molybdenum triple bond was formed by protonation by the phenol of the tetrabond of dimolybdenum tetraacetate. However, ($Mo_2(OAc)_4$) in the presence of 4-chlorophenol is less active as a catalyst than $Mo(CO)_6$.

Finally, we discovered that phenol can be advantageously substituted by silanols to form an efficient co-catalyst in alkyne metathesis with $Mo(CO)_6$. With triphenylsilanol (4) or diphenylsilanediol (5) [(1)/$Mo(CO)_6$/silanol$=20/1/2$] the metathesis equilibrium was obtained after 16 h of reflux in octane under argon. In the case of the trisilanol-POSS (6),[6] the equilibrium was observed only after 20 h of reflux and needed more octane due to the poor solubility of (6) (Scheme 2).

Recently many reactions with transition metal complexes have been accelerated by microwave irradiation.[7] We tried to accelerate the metathesis of alkynes by microwave irradiation at 2450 MHz in a resonance cavity.[8] With phenol as cocatalyst, we did not obtain good results using octane due to the small absorption of microwave by the mixture. We obtained better results using propylene carbonate instead of octane. Propylene carbonate is a more polar solvent ($\varepsilon=69$ Debyes) than octane ($\varepsilon=2$ Debyes) and needed a powerful irradiation (5X1 min, 300 W), the temperature reached was 126°C.
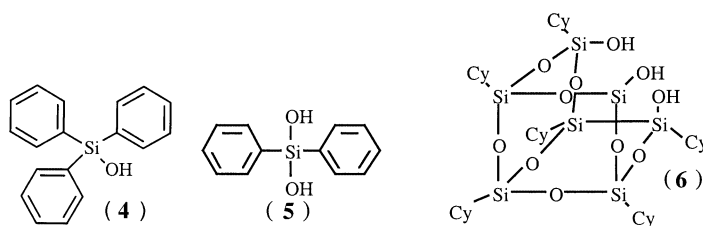
With silanols in octane the equilibrium was observed after only 10 min of irradiation[9] instead of the 16 h under reflux. With trisilanol (6) the equilibrium was observed after 20 min of irradiation instead of 20 h under reflux. We tested the catalyst [(4)+$Mo(CO)_6$] under microwaves with varying functionalised alkynes[4] in cross metathesis.[8] The equilibrium was observed in all cases after less than 15 min of irradiation. With the very sensitive enone (7g) the equilibrium was observed with [(4)+$Mo(CO)_6$], but we did not observe metathesis with the phenol catalyst [$Mo(CO)_6$+ClC_6HOH].

With (7f) we observed the shift of equilibrium, and a quantitative yield of (2) was obtained due to the elimination of volatile hexamethyldisilylacetylene (8f) (Scheme 3).

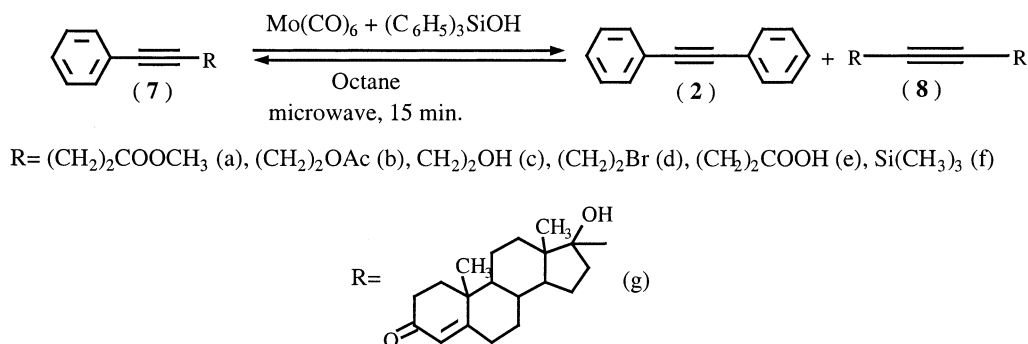In conclusion silanol [triphenylsilanol (4) and diphenylsilanol (5)] with $Mo(CO)_6$ is readily available, particularly efficient and functionally tolerant catalyst for alkyne metathesis. The metathesis is very rapid under microwave irradiation.

Acknowledgements

Scheme 2. Silanols used as cocatalyst with $Mo(CO)_6$.

R= $(CH_2)_2COOCH_3$ (a), $(CH_2)_2OAc$ (b), $CH_2)_2OH$ (c), $(CH_2)_2Br$ (d), $(CH_2)_2COOH$ (e), $Si(CH_3)_3$ (f)

Scheme 3. Metathesis of functionalised alkynes under microwave irradiation.

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9. *Typical procedure for alkyne metathesis*: A mixture of 4-methoxytolan (416 mg, 2 mmol), $Mo(CO)_6$ (28 mg, 0.1 mmol) and triphenylsilanol (55 mg, 0.2 mmol) was introduced in octane (5 ml) under an argon atmosphere in an Ace pressure tube (38 mL) with a security valve (10 atm). The mixture was irradiated in a microwave resonance cavity Synthewave 402 Prolabo at 200 W for a period of 10 min. The mixture turned black. The crude reaction product was filtered on silica gel and analysed by GC (SE30, 250–280°C). The products were separated by preparative TLC on silica (AcOEt/cyclohexane: 1/9): 4,4′-dimethoxytolan (**3**) ($R_f = 0.34$), 4-methoxytolan (**1**) ($R_f = 0.5$) and tolan (**2**) ($R_f = 0.85$). The products were identified by NMR, IR and mass spectroscopy.