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***In situ* Mo(CO)₆-based catalysts for alkyne metathesis: silanols vs phenols as co-catalysts under thermal and photochemical activation.**

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ABSTRACT

A systematic study on the use of silanols and phenols as effective activators in Mo(CO)₆ – based catalytic systems for the metathesis of 4-decyne and 1-phenyl-1-propyne is reported. In comparison with traditionally used phenols, aryl-substituted silanols exhibit high activating potential of molybdenum species even at lower concentrations (2 mol% of Mo(CO)₆ and 4-20 mol% of silanol depending on the alkyne) at toluene reflux. Silylated phenols and silanols are also proved to be suitable as co-catalysts. Additionally, the Mo(CO)₆/silanol catalytic system is shown to be efficiently activated by UV-irradiation at room temperature, whereas it is less effective for the metathesis reactions performed in the presence of phenols.

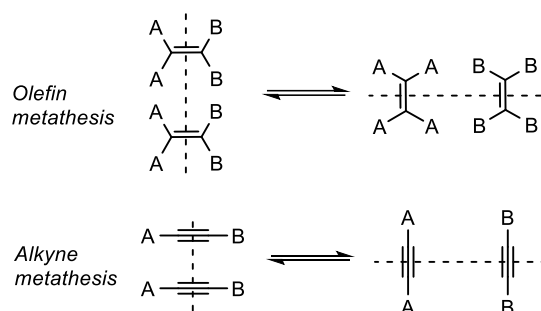
Highlights.

- Aryl-substituted silanols are versatile co-catalysts for Mo(CO)₆ *in situ* based alkyne metathesis catalysts.
- Reducing the co-catalyst / Mo molar ratio as low as 2 is possible for alkyl di-substituted alkynes.
- Room temperature alkyne metathesis is performed using photochemical activation.
- Silylated phenols and silanols are found to be efficient alternative co-catalysts.

Keywords : alkyne, metathesis, molybdenum, phenols, silanols, photochemistry, activation.

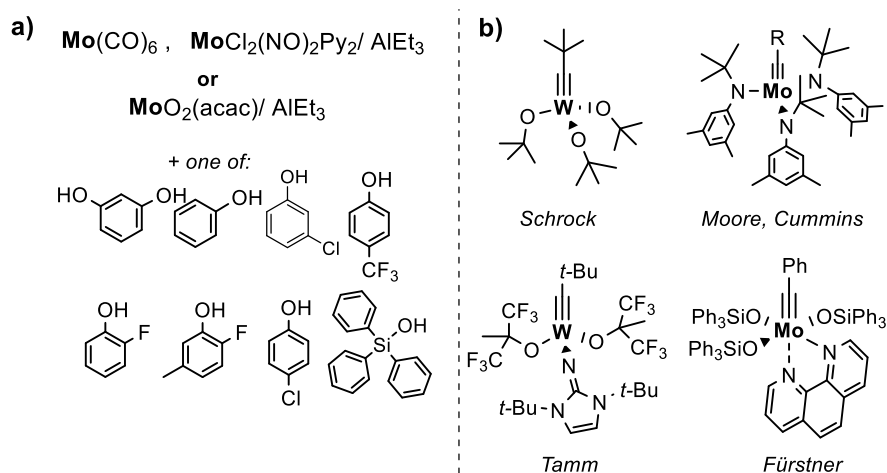
1. Introduction

First reported in 1968 as a heterogeneous process,[1] alkyne metathesis, a reaction analogous to the better known olefin metathesis (Scheme 1), remained in the shade until the break of new millennium gave it a chance.[2] Initially, homogeneous catalytic systems for this reaction consisted of molybdenum hexacarbonyl and resorcinol.[3] Further improvements of this Mo(0)-based system have been made, using thermal activation and high concentration of phenols.[4] In contrast, high oxidation state Mo(VI) alkylidyne complexes have been developed, and the best up-to-date summaries of their development and applications in alkyne metathesis have been presented by Fürstner [5] and Tamm.[6]



Scheme 1. General scheme for self-metathesis reactions.

(Pre)catalysts for alkyne metathesis can be divided into two main classes (Scheme 2). The first one is represented by the original homogeneous system described above, and is referred to as the *multicomponent, instant* or *in situ* catalytic system (a), which has been improved to provide better turnover numbers (up to 200 h⁻¹) at toluene reflux. Another interesting version of multicomponent catalytic systems consisting of higher oxidation state molybdenum sources MoO₂(acac) or MoCl₂(NO)₂Py₂/AlEt₃/ArOH or silanols has also been described, leading to much higher reaction rates (up to 40 s⁻¹).[7,8] The catalysts represented by a Schrock tungsten alkylidyne complex and a variety of molybdenum congeners constitute the second class of *well-defined* catalysts (b). They are known for their exceptional catalytic activity but some of them suffer from high sensitivity towards oxygen and moisture.



Scheme 2. Examples of (pre)catalysts used in alkyne metathesis.[9–14]

Although relying on generally higher temperature experimental conditions, multicomponent catalytic systems have found several remarkable uses, especially in dynamic covalent chemistry [15–18], total syntheses of natural products [19–23], and material chemistry of arylene-ethynylene polymers.[24,25] Compared to alkene metathesis, these approaches benefit from the alkyne intrinsic lack of stereochemistry, which simplifies the outcome in term of product distribution.

The fact that $\text{Mo}(\text{CO})_6$ -based catalytic systems are still in use relies on the *off-the-shelf* character of the components at exceptionally low price, even taking into account relatively high molybdenum content and co-catalyst loadings (stoichiometric or even super-stoichiometric). In most applications and traditional catalysts' compositions, phenol and its derivatives have been used as activators. In contrast, reports describing silanols as capable of performing this function have been very scarce.[26,27]

This communication is aimed at experiments comparing the activity of silanols and phenols derivatives as co-catalysts in $\text{Mo}(\text{CO})_6$ *in-situ* catalytic systems. The choice of these silanols has been dictated by taking into consideration the successful results obtained by Fürstner's group on 1-phenyl-1-propyne metathesis, where a screening was made reacting a variety of potassium silanulates with a tribromo alkylidyne complex for the *in-situ* synthesis of siloxy-molybdenum carbynes.[28] Furthermore, looking at the possibility of reducing the amount of co-catalyst will be systematically checked and a photochemical approach for activating these systems at room temperature will be described, The results will show that the choice of the best co-catalyst will depend on the aliphatic or aromatic structure of the alkyne, as well as on the activation mode of these *in situ* catalysts.

2. Experimental

2.1. General considerations

All operations were conducted under argon atmosphere using standard Schlenk techniques. Toluene and tetrahydrofuran (Merck) were purified by distillation over sodium and benzophenone and degassed in the freeze-pump-thaw cycle. The compounds 4-decyne (Alfa Aesar), 1-phenyl-1-propyne (Sigma-Aldrich), and decane (Sigma-Aldrich) were vacuum-distilled over calcium hydride and stored under inert atmosphere. Commercial silanols (Sigma-Aldrich) were dried by applying vacuum for a prolonged time (note: applying heat under these conditions may result in their condensation). Hexacarbonylmolybdenum (Sigma-Aldrich) was sublimed *in vacuo*. The glassware was dried by heating under vacuum with a hot air gun to approximately 200 °C (measured with an IR pyrometer). UV-activated reactions were performed in a quartz reaction flask and irradiated using Opsytec Dr. Groebel GmbH LQ-400 UV irradiation system. GC analyses were performed on a Bruker 436-GC gas chromatograph with a TCD detector using decane as reference. GC-MS analyses were performed on either Bruker Scion 436-GC with Bruker Scion SQ mass detector or Varian 450 GC with Bruker 320-MS TQ detector.

2.2. Synthesis of dimethyl(naphthyl)silanol

A two-neck round-bottom flask was charged with 0.486 g Grignard-grade magnesium, equipped with a rubber septum and a condenser with inert gas/vacuum adapter and evacuated. After refilling with argon, 10 mL of tetrahydrofuran and 86 μL (1 mmol) of 1,2-dibromoethane were added. The mixture was gently heated to activate magnesium surface. After cessation of ethene evolution, another 30 mL of tetrahydrofuran were added followed by 1.67 mL (15 mmol) of chlorodimethylsilane. The mixture was stirred for 30 minutes. Next, 1.40 mL (10 mmol) of 1-bromonaphthalene was added dropwise, while the flask was cooled in a cold water bath. The mixture was stirred overnight under argon flow. After completion of the reaction, the excess of chlorodimethylsilane was neutralized with a small amount of isopropanol and the volume of the mixture was reduced to approximately 20 mL. Then 30 mL of hexane were added and the slurry was filtered through Celite. The filtrate was evaporated on a rotary evaporator and dried *in vacuo*, resulting in 1.42 g (76%) of a viscous oil of sufficient purity (95%; GC-MS). The whole amount of dimethyl(naphthyl)silane was then oxidized using a known procedure.[29]

^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.28 (m, 1H), 7.89 (m, 2H), 7.79 (dd, 1H), 7.51 (m, 3H), 2.09 (s, 1H), 0.6 (s, 6H)

^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 136.65, 136.30, 133.09, 132.97, 130.11, 128.73, 127.84, 125.74, 125.24, 124.74, 1.05

2.3. Alkyne metathesis

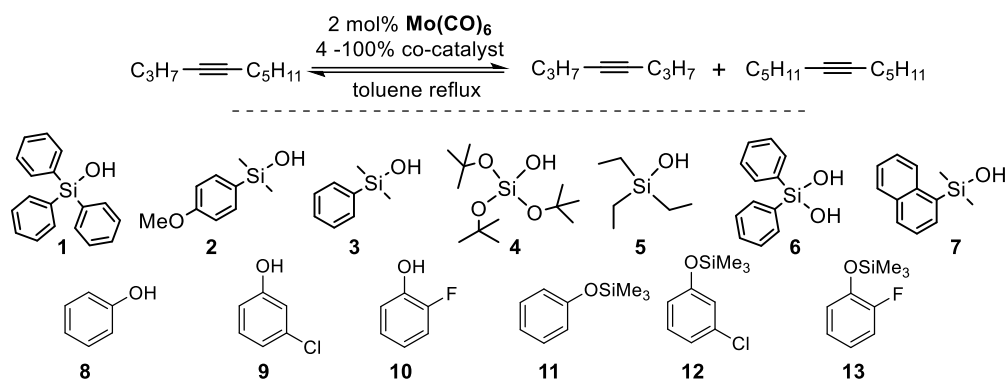
A round-bottom flask with an incorporated air condenser and threaded side arm closed with a bored cap equipped with a silicone septum was dried under vacuum and charged with 2 mL toluene. Next, appropriately calculated amounts of co-catalyst and 1 mmol of alkyne were added and dissolved along with 100 μ L of decane. A suitable amount of $\text{Mo}(\text{CO})_6$ was then added. The solution was degassed by gently applying vacuum and refilling with argon and a reference sample was taken. In the thermally activated metathesis, the flask was next put in an oil bath heated to 115 $^{\circ}\text{C}$ to ensure boiling of toluene. Alternatively, in photochemically activated metathesis, the flask was put on a magnetic stirrer with the light guides of the UV irradiation system aiming at the solution from the bottom. Aliquots were taken in the course of the reaction and analyzed using gas chromatography to determine the conversion of the alkyne vs time. The last sample was analyzed by GC-MS to determine the final contents of the reaction mixture. Following is a typical example of 4-decyne metathesis:

The flask was charged with 2 mL of toluene, 100 μ L of decane, 180 μ L (1 mmol) of 4-decyne, and 11 mg (0.04 mmol) of triphenylsilanol. Upon dissolution of the silanol, 5.3 mg (0.02 mmol) of hexacarbonylmolybdenum was added. The mixture was gently degassed by applying vacuum. After refilling the flask with argon, a reference sample was taken. The flask was then put in an oil bath pre-heated to 115 $^{\circ}\text{C}$ and heated for 120 min with strong stirring.

3. Results and discussion

3.1. 4-decyne metathesis under thermal activation.

Several silanols were chosen for first catalytic trials using 4-decyne as the substrate: commercial triphenylsilanol **1**, (4-methoxyphenyl)dimethylsilanol **2**, dimethylphenylsilanol **3**, tris(*tert*-butoxy)silanol **4**, triethylsilanol **5**, and diphenylsilanediol **6** as well as custom-made dimethyl(naphthyl)silanol **7**. They were compared with typically used phenols **8-10** as their silylated derivatives **11-13** for the same reaction, using different co-catalysts/molybdenum ratio (Scheme 1, Table 1)



Scheme 1. Screening of aryloxy- and siloxy-based co-catalysts for 4-decyne metathesis.

Table 1. Comparison of efficiency of different co-catalysts in self-metathesis of 4-decyne.^a

Co-catalyst	ZOH/Mo (mol/mol)	Conv. ^b 30 min	Conv. 60 min	Conv. 120 min	TR(h ⁻¹) ^c
Ph ₃ SiOH 1	50	1	7	22	8
	2	6	20	38	10
	5 ^d	3	9	17	9
(4-MeOC ₆ H ₄)Me ₂ SiOH 2	50	44	50	52	44
	2	20	40	49	20
Me ₂ PhSiOH 3	2	22	45	-	22
(Me ₃ SiO) ₃ SiOH 4	50	0.5	1.4	3	0.5
Et ₃ SiOH 5	50	5	14	24	7
Ph ₂ Si(OH) ₂ 6	2	9	22	36	11
Me ₂ (Napht)SiOH 7	2	18	47	52	29
PhOH 8	50	17	45	51	28
	2	16	26	31	16
3-ClC ₆ H ₄ OH 9	50	45	51	51	45
	10	51	51	51	51
	2	41	45	-	41
2-FC ₆ H ₄ OH 10	50	11	37	52	26
	10	34	43	54	34
C ₆ H ₅ OSiMe ₃ 11	50	6	20	30	14
3-ClC ₆ H ₄ OSiMe ₃ 12	50	27	34	53	27
	10	28	42	51	28
2-FC ₆ H ₄ OSiMe ₃ 13	50	5	6	33	14
	10	6	9	50	20

(a) Conditions: solvent toluene; reflux; 0.5 M in 4-decyne, 2 mol% Mo(CO)₆ (b) 4-decyne conversion, determined by GC using *n*-decane as internal standard. (c) moles 4-decyne converted per mole Mo per hour, calculated from the highest reaction rate using conversion vs time data. (d) Mo loading 1 mol%

These results indicate that all aromatic silanols are successful in this reaction, in particular **2** and **3**, as well as the naphtyldimethylsilanol **7** whereas **4** and **5** lead to a significantly less efficient system. It is worth noting that this reaction reaches equilibrium more rapidly when using phenols

as co-catalysts and that 3-chlorophenol **8** is the best candidate for this reaction (turnover rate 41 h⁻¹ at a co-catalyst /Mo ratio as low as 2)). Another interesting result to highlight is that O-silylated phenols are also suitable: although they are ca 50% less efficient as co-catalysts than their parent hydroxy compounds, they allow reaching the equilibrium within 2h reaction time. Typically, using the silylated fluorophenol **13**, the corresponding activated system was found to present an induction period before becoming as reactive as its hydroxylic **10** precursor, whereas this behavior was not observed with co-catalyst **12**. This unprecedented result opens the way to a new generation of instant catalysts useful in applications where the presence of phenols or silanols are redhibitory due to the presence of acidic OH groups.[22] It has to be stressed that these results were achieved only when rigorously oxygen-free and dry conditions were applied.

3.2. 1-phenyl-1-propyne metathesis under thermal activation

Next, aromatic-substituted 1-phenyl-1-propyne was subjected to metathesis as the second, more demanding model substrate. Screening experiments depicted in Table 2 show that the efficiency in the metathesis of 1-phenyl-1-propyne is more sensitive to a decrease in the amounts of co-catalyst than that of 4-decyne.

Table 2. Comparison of efficiency of different co-catalysts in metathesis of 1-phenyl-1-propyne. ^a

Co-catalyst ZOH	ZOH/Mo (mol/mol)	Conv. 30 min(%)	Conv. 60 min(%)	Conv. 120 min(%)	TR(h ⁻¹)
1	50	3	23	47	20
	10	6	41	85	35
	2	2	3	3	-
2	50	18	73	80	55
	10	9	32	53	21
3	2	6	27	49	21
6	50	51	76	86	51
	10	23	44	63	23
	2	13	24	32	13
7	50	22	82	84	60
	10	23	62	79	39
8	2	10	14	17	-
9	10	0	15	28	-
	2.5	1	2	4	-

(a) Conditions: same as in Table 1. 1-phenyl-1-propyne as substrate, catalyst loading 2 mol%.

Indeed, when the co-catalyst amount was reduced, high alkyne conversion was achieved only when **1** or **7** were used as co-catalyst. Noteworthy, these co-catalysts require the use of 20 mol% of silanol for the reaction to proceed efficiently. Surprisingly, although the first report on metathesis using Mo(CO)₆-phenols used paratolylphenylacetylene as substrate, phenols as co-catalysts at low ArOH/ Mo ratio were by far less reactive and also unselective: even if a low conversion of 1-phenyl-1-propyne was observed, cyclotrimerization and oligomerization took

place instead. An explanation of this discrepancy could come from the fact that being less sterically hindered than their siloxy homologs, aryloxy-methylcarbyne species are prone to side reactions such as 2-butyne polymerization, as evidenced earlier on the use of several *in situ* prepared triaryloxymolybdenum(VI) methylidyne during metathesis of the same substrate.[12] Conversely, diphenylsilanediol **6** turned out to be relatively effective using low co-catalyst loading.

3.3. Metathesis under photochemical activation.

The study of photo-dissociation of hexacarbonyl molybdenum(0) was one of the founding stones of transition metal photochemistry and it since then still provides valuable access to substituted molybdenum carbonyl derivatives.[30] Building on our former, seminal experiments using UV irradiation to activate Mo(CO)₆/ArOH catalysts for 4-nonyne metathesis,[27] we proceeded with the study of these dual Mo(CO)₆/ZOH pre-catalyst combinations in alkyne metathesis under UV irradiation.

3.3.1. 4-decyne metathesis under photochemical activation

Model reaction systems were essentially the same as for thermally-activated metathesis: Selected results using 4-decyne as the substrate at room temperature are given in Table 3.

Table 3. 4-decyne metathesis under UV using selected co-catalysts with different loadings.

Co-catalyst ZOH	ZOH/Mo (mol/mol)	Conv. 30 min (%)	Conv. 60 min (%)	Conv. 120 min (%)	TR (h ⁻¹)
1	20	34	46	49	34
	10	16	29	30	16
	5	26	27	27	26
2	20	20	34	35	20
	10	17	26	29	17
	5	11	16	18	11
3	30	31	48	50	31
	20	24	32	32	24
	10	23	40	43	23
	5	8	8	8	8
6	20	8	10	10	8
8	50	3	6	9	3
9	50	3	5	5	3

(a) Conditions: toluene (r.t.), 0.5M in 4-decyne, catalyst loading 2 mol%.

Most interestingly, using such an approach, the reaction proceeds under significantly milder conditions than in the case of thermal activation (room temperature vs 110 °C). As shown in the present study, the conversion of 4-decyne was much more efficient in the presence of silanol co-catalysts. The use of phenols **8** and **9** lead to poor catalytic activity under these conditions, whereas they were shown to be efficient when using higher molybdenum content.[27] It is also

worth noting that UV-activated metathesis stops after approximately 60 minutes- or even before at low co-catalyst loading - and no further significant increase in conversion is observed beyond this point. Its final value seems to be directly dependent on the amount of silanol co-catalyst used, as best shown by the examples involving co-catalyst **3** (Figure 1).

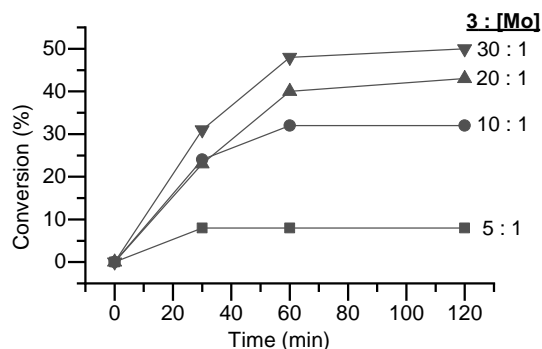


Figure 1. Kinetic profiles of UV-induced metathesis of 4-decyne co-catalyzed by **3**. Conditions: toluene (r.t.), 0.5M in alkyne; $[C\equiv C]:[3]:[Mo] = 1:variable:0.02$.

3.3.2. 1-phenyl-1-propyne metathesis under UV activation.

As emphasized in Table 4, metathesis of 1-phenyl-1-propyne required much higher Mo content to occur. This could be attained at acceptable rates and conversion using 5 mol% molybdenum and equimolar amounts of co-catalyst (with respect to the substrate). In this case again, silanols **1** and **3** are the best candidates.

Table 4. 1-phenyl-1-propyne metathesis under UV using selected co-catalysts with different loadings. ^a

Co-catalyst	Mo loading (mol%)	Conv. 30 min	Conv. 60 min	Conv. 120 min	Average TR (h ⁻¹)
1	5	42	43	45	16
	2	19	26	32	19
2	5	8	10	11	2
	2	3	5	6	3
3	5	41	42	42	16
	2	6	7	9	6
6	2	11	13	13	13
8	5	8	15	15	8
8	2	5	5	8	5
9	5	4	6	8	1
9	2	0	0	3	0

(a) Conditions: same as in Table 1, 1-phenyl-1 propyne as substrate, 1 mol. eq. co-catalyst per substrate.

However, even in these cases, a maximum conversion of only 45% was achieved. Considering the evolution of the conversion of 4-nonyne vs time under identical conditions

(Figure 1), it appears that again, the conversion does not improve after 1h, indicating a catalyst deactivation. A tentative explanation of this catalyst decay may come from a separate experiment aimed at the analysis of the evolution of the Mo(CO)_6 content during irradiation. Following the Mo(CO)_6 decay vs time via UV-VIS spectroscopy shows indeed that a rapid decrease is observed within 60 min. (Figure 2). This indicates that the active species are produced and react rapidly under such conditions, but are short living.

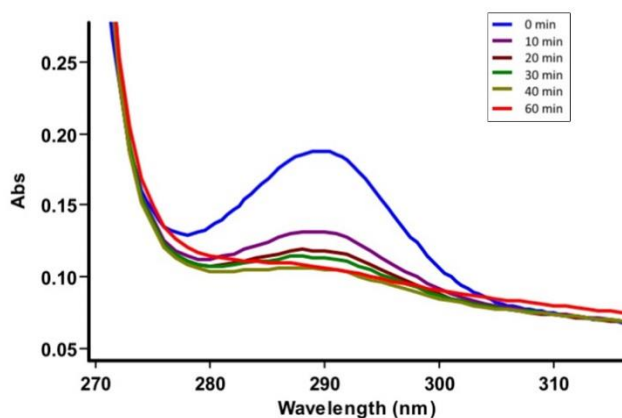


Figure 2. Mo(CO)_6 concentration decay vs time under UV irradiation.

Nevertheless, it is worth mentioning that using significantly milder conditions than classical ones, such a demanding substrate can be metathesized with promising performances.

4. Conclusion

In summary, alkyne metathesis using molybdenum hexacarbonyl as precatalyst is efficiently co-catalyzed by aryl-substituted silanols as benign and more versatile substitutes of phenol derivatives, using low co-catalyst/Mo ratio. In addition, such silanol-based systems are prone to be activated photochemically, giving rise to promising catalytic activities under milder conditions than that of the classical thermal protocol. Associated with the unprecedented use of silylated phenols as a new co-catalysts generation, these results open several avenues in the development of derived systems with potentially increased performances useful for synthetic applications in organic and polymer chemistry.

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