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ALKYNE METATHESIS CATALYSTS: SCOPE AND FUTURE.

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ABSTRACT

This paper presents the evolution of alkyne metathesis since the early discoveries, essentially from the catalyst point of view. It is shown that although well defined carbynes may be useful for this reaction, further work has been made, aimed at the synthesis of new catalysts or catalytic systems, based on molybdenum precursors , associated or not with phenolic co-catalysts. The major objectives have been to obtain more functional groups tolerants catalysts, for their application in organic synthesis, including RCM for further stereoselective hydrogenation of the triple bond in the cycle, as well as for polymerization of aromatic diynes.

Some insights into the possible mechanisms are given, and data relevant to the metathesis of terminal alkynes, a still challenging reaction where polymerization is occurring via the formation of deprotonated metallacyclobutadiene, are also presented and discussed.

1. Introduction

During ISOM16, for which this special issue of Journal of Molecular Catalysis is devoted, the contributions of R. H. Grubbs and R. R. Schrock, our Nobels for 2005, were devoted to alkene metathesis, as well as most of the other contributions from several authors, either looking at new and more efficient catalysts, in terms of both activity and tolerance to functional groups, or to their application in organic synthesis or polymerization.

However, although they are studied to a much lesser extent, other metathesis reactions have been the subject of some report in this meeting: alkane - a rather young reaction - and alkyne metathesis, the latter being known almost since the event of alkene metathesis.

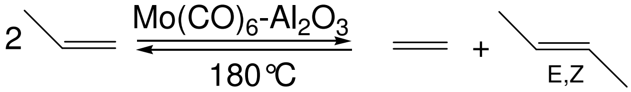
The availability of alkynes is probably one of the major features which have led to a much lower interest in that field than using alkenes. Nevertheless, after the discovery of triple bond metathesis homogeneous catalysts during the seventies –beginning of the eighties, a renewed interest, essentially governed by potential application in the synthesis of specialty polymers and in organic synthesis, has appeared in the late nineties.

Alkyne metathesis is nowadays what can be considered as a tool for people working in these fields. This review is aimed at giving the milestones which have to be considered as breakthroughs in this reaction from the catalysis point of view, together with some emphasis in the limitation and application of catalysts described so far in the literature.

2. Molybdenum based catalysts

2.1. Heterogeneous catalysts

Following their discovery related to the Triolefin Process using molybdenum carbonyl on alumina (eqn 1)[1], Banks and Bailey reported with Penella the first heterogeneous catalyst for alkyne metathesis in 1968, applying tungsten oxide on silica at 350°C for pent-2-yne metathesis with a 55% selectivity (eqn 2) [2].



(1)

$$2\ C_2H_5{-}{\equiv}{-}CH_3 \xrightleftharpoons[350\,°C]{WO_3\text{-}SiO_2} H_3C{-}{\equiv}{-}CH_3 + C_2H_5{-}{\equiv}{-}C_2H_5 \quad (2)$$

The same catalyst applied to a terminal alkyne such as pent-1-yne has been found to produce exclusively aromatic trimers [3], whereas a $CoO\text{-}MoO_3\text{-}SiO_2$ catalyst has been claimed to be selective in metathesis of this substrate [4].

In our hands, other catalysts based on molybdenum oxide on silica have been shown to be much more selective towards disubstituted alkynes [5], the most efficient being the oxide obtained via a previous grafting of tetrakis π-allyl-molybdenum on a previously pretreated silica surface [6,7]. This surface organometallic precatalyst, suggested to consist of a monolayer of $Mo(\Pi\text{-allyl})_2(OSi\equiv)_2$ surface species was by itself efficient for hex-2-yne metathesis, but upon oxidation and further pre-treatment under nitrogen at high temperature (550°C), and cooling down at the reaction temperature(350°C) gave unprecedented activities and selectivities. This catalyst, where molybdenum is linked to silica via $Mo\text{-}O\text{-}Si\equiv$ bonds, gave a 95% selectivity in metathesis compounds oct-4-yne and but-2-yne with activities 3 times higher than those observed on conventional $MoO_3\text{-}SiO_2$ catalysts prepared by classical impregnation [6,7]. This remarkable enhancement led us to conclude that the formation of Si-O-Mo bond at the silica surface was essential for the formation of the active species, and that such a linkage should occur when using heterogeneous molybdenum hexacarbonyl on silica catalysts, which were also shown to be active for this reaction at temperatures as low as 220°C [6].

This result has been the origin of our first attempts related to the use of such systems in a liquid phase: heating a mixture of molybdenum hexacarbonyl with suitably pre-treated silica and paratolylphenylacetylene ($C\equiv C/Mo = 33$) led in less than 1 hour to the corresponding metathesis compounds at equilibrium at 160°C [6,7].

2.2. Homogeneous catalyst

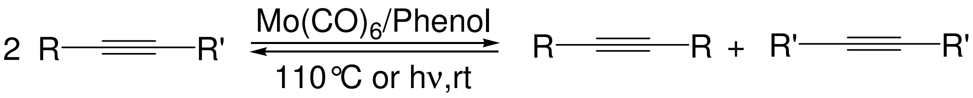
2.2.1. The $Mo(CO)_6$/ArOH based catalyst

More than three decades ago, the above results initiated our attempts at the use of molybdenum hexacarbonyl and OH containing organic compounds: the first successful reaction was done using resorcinol in decaline as solvent at 160°C (eqn 3) [9].

$$2\ \text{p-tolyl}{-}{\equiv}{-}\text{Ph} \ \overset{\text{Mo(CO)}_6\text{/Resorcinol}}{\underset{\text{Decaline, 160°C}}{\rightleftharpoons}} \ \text{Ph}{-}{\equiv}{-}\text{Ph} + \text{p-tolyl}{-}{\equiv}{-}\text{p-tolyl} \qquad (3)$$

This was followed by reactions conducted at 110°C using phenol as cocatalyst and extended to the use of (mesitylene) $Mo(CO)_3$ as the catalyst precursor [8]. The reaction needs large quantities of this hydroxy compounds – generally in equimolar amounts with the substrate or even higher– as the rate has been shown to be first in order in this "co-catalytic" component and can be applied to either aromatic or alkyl disubstituted alkynes. The latter are much more readily transformed into the corresponding equilibrium mixture: during separate homometathesis experiments or cross metathesis reaction the reactivity of hep-3-yne has been found 12 times higher than that of paratolylphenylacetylene [8, 10, 11].

It has also been shown that under photochemical activation, the reaction could occur at room temperature (eqn 4) [10,11].



$$2\ R{\equiv}R' \xrightleftharpoons[110^{\circ}C\ \text{or}\ h\nu,\text{rt}]{Mo(CO)_6/\text{Phenol}} R{\equiv}R + R'{\equiv}R' \qquad (4)$$

The use of different co-catalysts leads to different activities: 3-chlorophenol is 14 times more efficient than phenol itself, and other acidic proton cocatalysts such as trifluoroethanol, dihydroxydiphenylsilane and to a lesser extent pyrrole are also suitable; heterogenizing resorcinol on silica after chloromethylation gave also an active, grafted phenolic recoverable co catalyst, as well[1] [11].

Experiments aimed at the knowledge of the role of phenol have been performed, showing that preheating a $Mo(CO)_6$/PhOH mixture before introducing the alkyne led to inactive catalysts,-a result which has been confirmed later by several authors -whereas such a pre-reaction conducted at 110°C between $Mo(CO)_6$ and the alkyne gave a system which undergo metathesis after cooling to room temperature followed by 3-chlorophenol introduction [10].

The same results were obtained after UV irradiation of the $Mo(CO)_6$-alkyne mixture at room temperature: the metathesis reaction started then readily upon 3-chlorophenol addition and was still occurring when the irradiation was stopped [10,11]. Infrared studies were conducted, and have clearly shown that hydrogen bonding between the triple bond and the acidic proton was occurring. This will be taken into account in the section related to the mechanism of the reaction [10,11].

Following this results, some other molybdenum carbonyl complexes have been synthesized and compared in terms of activity, using non-4-yne as substrate.

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[1] **Reactions using silicon grease and molybdenum carbonyl precursors also gave some metathesis activity, due to the presence of some remaining SiOH groups: one must keep in mind this behaviour upon using catalytic precursors such as amido molybdenum or tungsten complexes which may react with this "reactive" material used in conventional glass equipments, especially upon using high temperature reactions and long reaction times**.

First reactions compared mesitylene molybdenum tricarbonyl and $Mo(CO)_6$, using 5 mol% catalyst in nonane at 120°C and a PhOH/C≡C ratio of 10: the former complex was found 4 times as active as $Mo(CO)_6$. Another series of molybdenum carbonyls was tested and showed again that the activation was ligand dependent However, the use of an aromatic solvent strongly affected the reactivity of the aromatic $ArMo(CO)_3$ complex (table 1) [12].

Table 1: Comparative results using different molybdenum carbonyl catalytic precursors during non-4-yne metathesis [12].

Catalytic precursor	$Mo(CO)_6$	(Norbornadiene)-$Mo(CO)_4$	(Cycloheptatriene)-$Mo(CO)_3$	(1,3-cyclohexadiene)$_2$-$Mo(CO)_2$	(Mesitylene)-$Mo(CO)_3$
Activity (h^{-1})	120	312	216	240	6

Conditions: solvent= toluene (10 ml); [C≡C] = [Mo]= 0.1M; [C≡C]/Mo= 100; T= 110°C.

Obviously, the substitution of molybdenum carbonyls by either dienes, trienes or aromatics gives rise to higher reaction rates, and prompted us to check other related systems without cmonoxide ligands.

2.2.2. The $MoO_2(acac)_2/AlEt_3/ArOH$ system

Following the idea that Mo° complexes associated with phenol as co-reagent or co-catalyst would be good candidates for alkyne metathesis, we decided to look at the use of the Chatt's complex $Mo(dppe)_2(N_2)_2$ as catalytic precursor [12]. Successful attempts upon using this catalyst - again with a large excess of phenol - at room temperature prompted us to apply the synthetic procedure leading to this complex to discover new in situ catalytic systems.

Reactions were then performed using $O_2Mo(acac)_2$ as precursor and 6 eq. of $AlEt_3$ or $Al(isobutyl)_3$ without phosphine , and using phenol as co-reactant: the results have been optimized in such a way that metathesis occurred readily at room temperature. In table 2 are given results related to the use of this system at toluene reflux, where activities as high at 40 turnovers per second are observed using non-4-yne as substrate (0.05% catalyst). Furthermore, some functionalized alkynes were successfully metathesized [13].

Table 2: Metathesis of unfunctionalized and functionalized disubstituted alkynes catalysed by molybdenum complexes[a] [13].

Alkyne	[alkyne]/[Mo]	[PhOH]	Activity min^{-1}
Bu-C≡C-Pr	2000	0,1M	2400

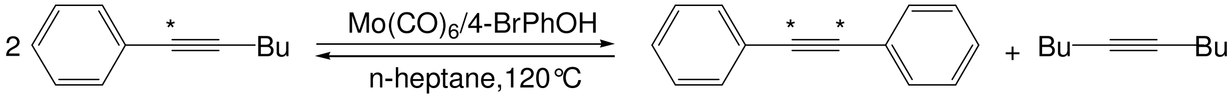
$Ph-C\equiv C-C_6H_4Me$	100	1M	6,4
$CH_2=CH-CH_2-C\equiv C-Bu$	1000	0,1M	28
$Cl-(CH_2)_3-C\equiv C-Et$	1000	0,1M	1015
$MeCO_2-(CH_2)_2-C\equiv C-Bu^b$	100	1M	0,2

^{a}Conditions: solvent = toluene; temperature = 110°C; [Mo] = 10^{-3} M; Al/Mo = 6/1.^{b} $Mo(CO)_6$-PhOH was used as catalyst.

Interestingly, the use of an allyl substituted alkyne also showed that the metathesis was entirely chemoselective, and that esters functionalized alkynes may also be metathesized on the $Mo(CO)_6$-PhOH catalyst.

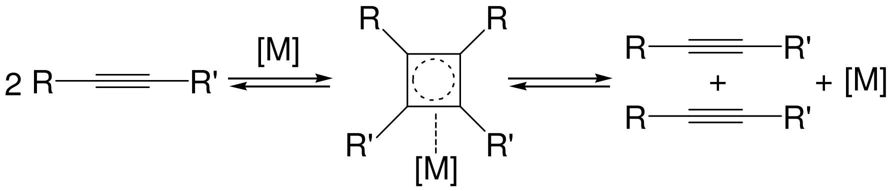
2.3. Mechanism using molybdenum/ArOH catalysts.

As for alkene metathesis, labeled experiments have been made to decide whether the process would occur via a transalkylation or transalkylidynation. The answer has been given upon using specifically labeled 1-phenyl-hexyne which gave labeled diphenylacetylene and 5-decyne (eqn 5) [14].



(5)

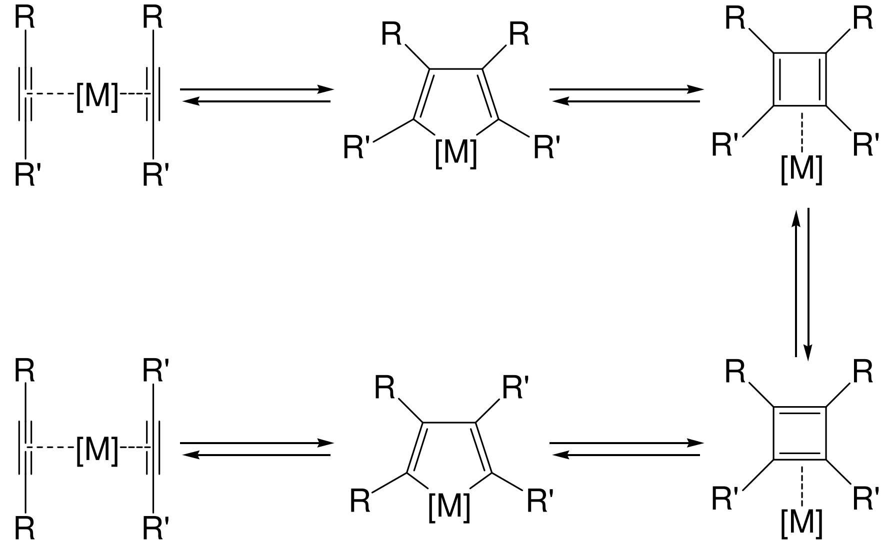
This redistribution is consistent with the first mechanism suggested by Penella, Banks and Bailey (fig. 1) where cyclobutadiene-metal complexes have been suggested (fig. 1) [2].



Scheme 1. η^4 cyclobutadiene metal complex mechanism [2]

Cyclobutadiene molybdenum complexes have been isolated from a reaction between paratolylphenylacetylene and molybdenum hexacarbonyl, but were considered to be too stable to suggest that this type of intermediate would be those involved in catalysis, due to too high reaction time and temperature for their decomposition [6].

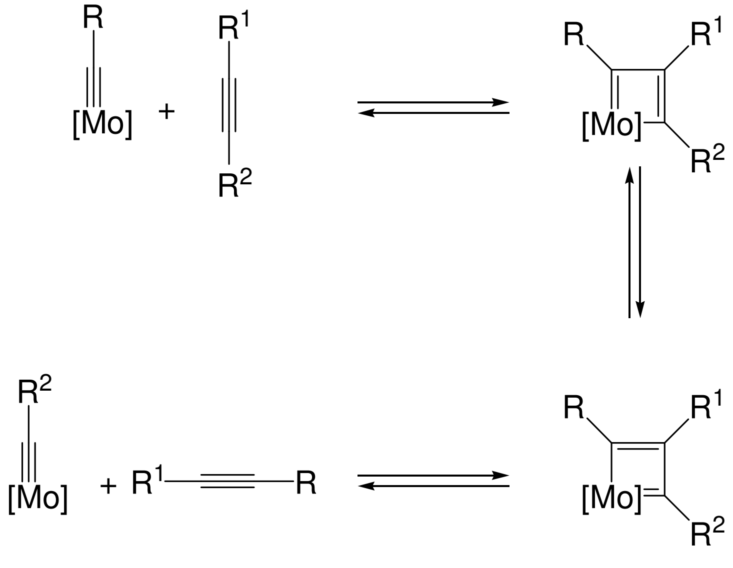
For this system, Mori et al. have also suggested that metallacyclopentadiene intermediates obtained via oxidative coupling may also intervene and isomerise via such cyclobutadiene-metal complexes (fig. 2). This proposal was made from results obtained on ortho hydroxyphenyl substituted alkynes, which led rather to trimerization product than metathesis ones [15a,b]; this hypothesis was supported later from experiments using cross reactions between diynes and a symmetrical alkyne, where a [2+2+2] cocyclisation was observed [15c]].



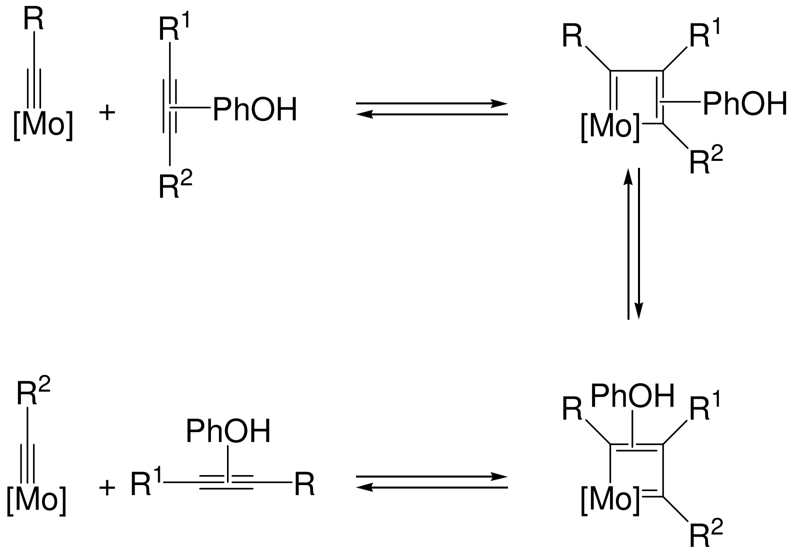
Scheme 2: metallacyclopentadiene type mechanism [15].

We had previously studied this reaction from the mechanistic point of view and proposed two alternative mechanisms.

The first one is a modified version of the former metallacyclobutadiene mechanism suggested by Katz as early as 1975 (scheme 3) [16] .



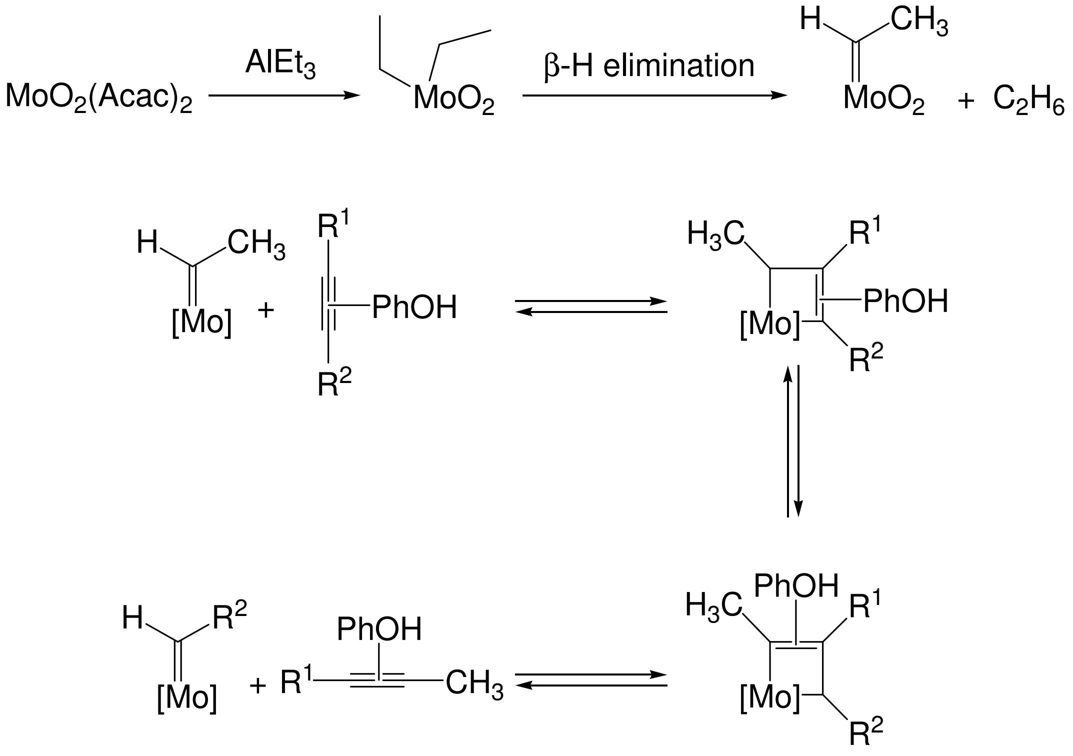
This proposal (scheme 4) was mainly due to the fact that hydrogen bonding between the hydroxyl group of the phenolic co-catalyst was clearly evidenced by IR studies: as far as the reaction rate was found to be first order in phenol [8, 12], the occurrence of an alkyne-phenol associated complex was considered as the key point giving rise to the metathetic process. As an hypothesis, the role of phenol was assigned to favor the isomerization of the metallacycle and avoïd trimerization [12].



Scheme 4.

~~Scheme 3.~~

However, a metallacarbene type mechanism has also been suggested, due to the fact that at least on $O_2Mo(acac)_2$-$AlEt_3$-PhOH catalysts, a α-H elimination process, as described earlier by Grubbs [17] could occur and generate metallacarbenes (scheme 5).



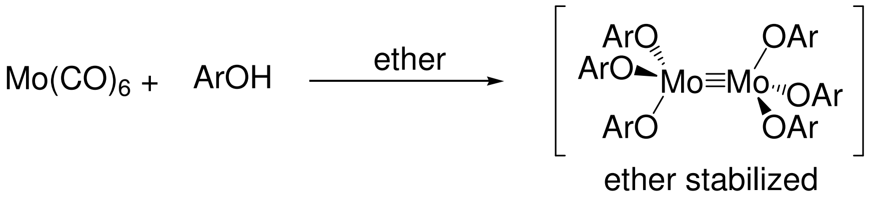
Scheme 5

This assumption has been further confirmed by a careful analysis of the initial products during non-4-yne metathesis using this system: hept-2-ene and hex-2-yne were initially produced.

The production of olefins arising from the alkylidyne moieties of the disubstituted alkyne to be metathesized was consistent with these alternative mechanistic hypothesis (Scheme 5) [18].

Such a mechanism has also been developed later to account for the production of putative metallacarbene intermediates during phenylacetylene polymerization on $Mo(CO)_6$-ArOH catalysts [19].

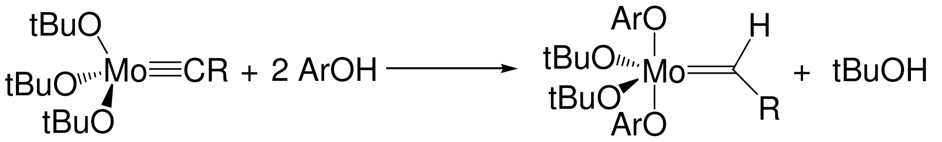
Recently, a stabilized metallacarbyne type mechanism has also been suggested upon using $Mo(CO)_6$-ArOH catalysts, via the incipient formation of a triple bond molybdenum dimer arising from oxidative addition of the phenolic reagent on molybdenum (eqn 6) [20].



(6)

This precursor would then react with the alkyne to produce the metallacarbyne propagating species. Even if the presence of ether is suggested to be the key point for stabilizing both the dimer and the metallacarbyne species, neither this bimetallic complex nor the metallacarbynes were identified or isolated from the reaction mixture.

Furthermore, another problem which arises in this context is that it is well established that metallacarbynes react readily with phenols to produce metallacarbenes (eqn 7) [21].


(7)

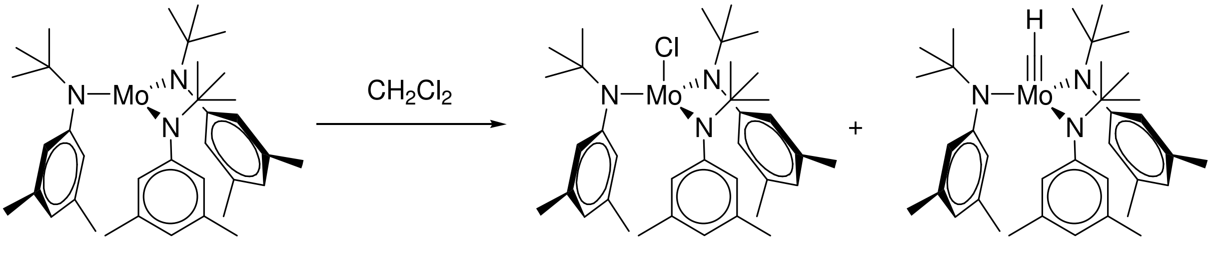
Lower oxidation state tungstacarbynes complexes such as $Br(CO)_3W{\equiv}CMe$ failed in our hands to provide metathesis products [12], which means that if it were so, catalysis should occur most probably on higher oxidation state species: one possibility would be that little amounts of highly reactive transient carbynes at higher oxidation state would be continuously formed from a reaction between molybdenum and phenol, and rapidly metathesize before they die.

In any case, the initiation process leading to these active species needs further experiments to be definitely proved.

2.4. Trisamido-molybdenum based catalysts

Based on the work done by Cummins related to nitrogen activation using trisamidomolybdenum complexes, Fürstner has shown that the use of the $Mo[N(tBu)(Ar)]_3$-CH_2Cl_2 combination was an active catalyst for alkyne metathesis [22].

The in-situ activation shown in scheme 6 can be done using either CH_2Cl_2, CH_2I_2 or $C_6H_5CHCl_2$.

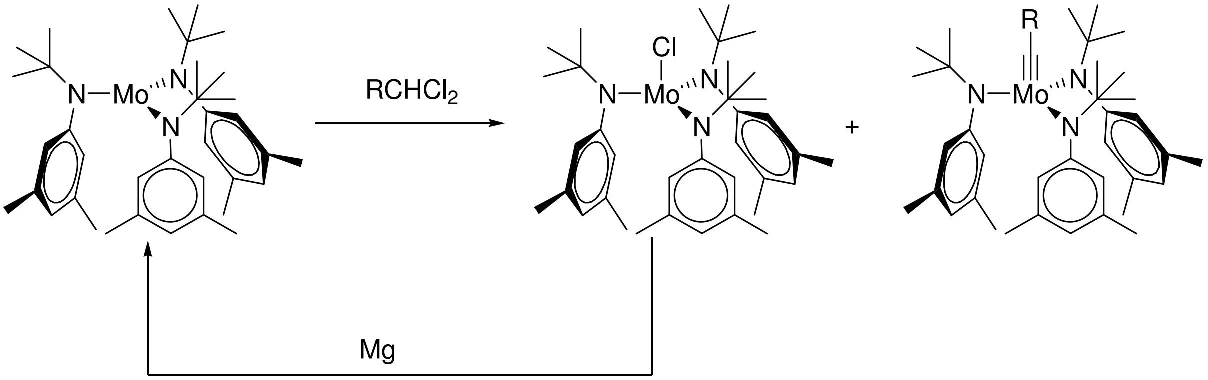


Scheme 6. Production of metallacarbyne species from a trisamidomolydenum precursor [22].

During this study, it has been shown however that the methylidyne carbyne was not the catalyst: only one turnover was observed using this carbyne as precursor, whereas the isolated $ClMo[N(tBu)(Ar)]_3$ complex gave 7 turnovers under the same conditions (10 mol % catalyst - 80°C-20 to 40 h.).

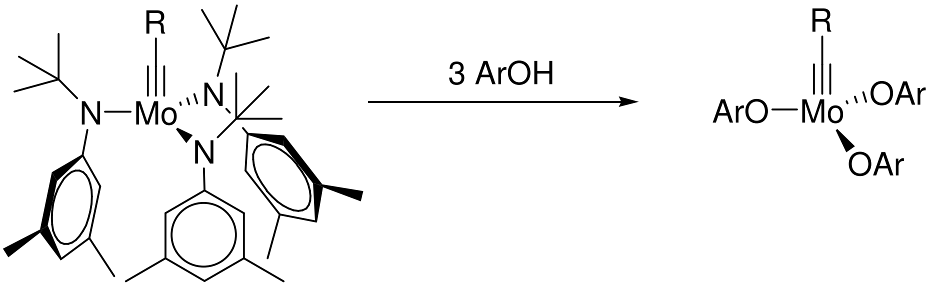
Although they are less reactive than the above $Mo(CO)_6$-ArOH and $MoO_2(acac)_2/AlEt_3$/ArOH catalysts [23], they have been shown to be much more tolerant to functional groups and applied for the synthesis of natural products [24].

An improvement of the catalytic behaviour of this system has been made by Moore [25], upon using the same trisamido molybdenum complex as starting material and gemdihalogenated derivatives, to produce metallacarbynes: magnesium addition in the solution allows to reduce continuously the chloride and therefore to produce the metallacarbyne species quantitatively after several reduction steps (scheme 7).



Scheme 7. Continuous generation of metallacarbyne species from trisamido molybdenum complexes [25].

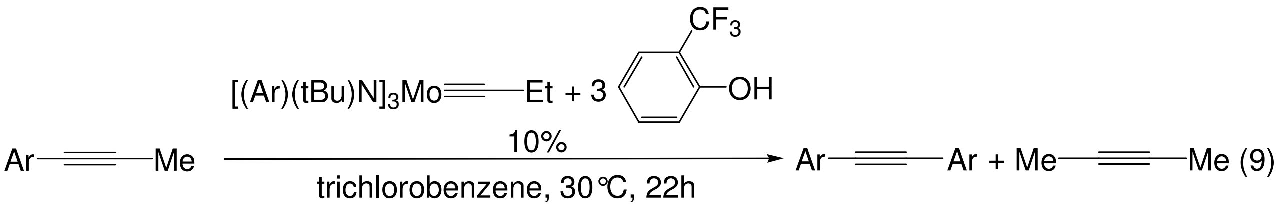
As stated before, these catalysts are not very active, but have been used as precursors for phenoxy-molybdenum carbyne via alcoholysis which have been shown to be more efficient: the reaction temperature could be reduced to 30°C (vs 80°C for the trisamido complexes (eqn 8) [26].



(8)

The use of the 2-trifluoromethylphenoxy derivative allowed to undergo metathesis of aromatic alkynes bearing nitriles, amines, aldehydes, and amino groups at 30°C, but again a 10 mol % catalyst and long reaction times (22 h) were generally used (eqn 9, table 3);

removal of but-2-yne from the reaction mixture allowed to enhance the yields starting from methyl substituted aromatic alkynes.



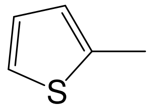
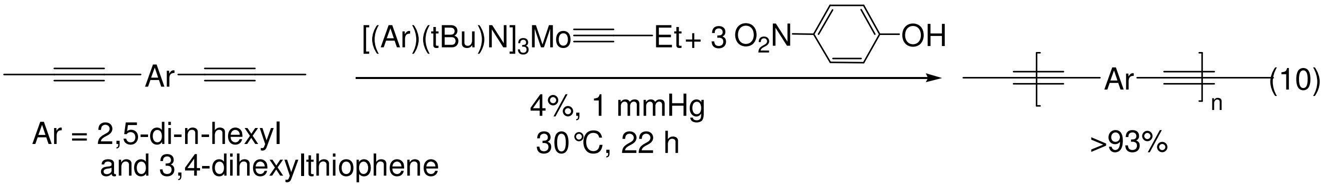
Ar	p-CNPh	p-NMe_2Ph	p-OMePh	p-CF_3Ph	p-CHOPh	
Yield %	37	76	83	51	47	<5

Table 3: Metathesis of various $\mathrm{ArC{\equiv}CR}$ type alkynes under 1 mmHg.

Another application of this system has been the use of α,ω diynes to undergo polymer formation via removal of but-2-yne (eqn 10).



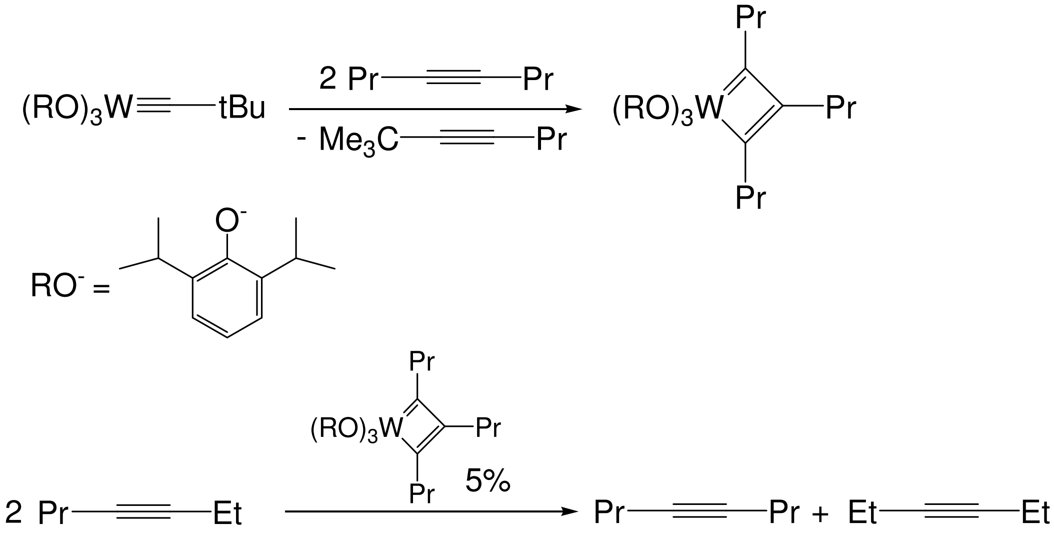
3. Well defined carbyne based catalysts.

Following Chauvin mechanism's proposal related to the occurrence of metallacarbene species as catalytic moieties for olefin metathesis, tremendous efforts were made by several groups aimed at the isolation and use of metallacarbenes in this reaction. The synthesis of high oxidation state metallacarbenes by Schrock has led to that of metallacarbynes, which had been previously suggested as potential active species for alkyne metathesis [16]. In that context, one might remind some earlier work by E.O Fisher, who by mixing and heating at 40°C $\mathrm{Br(CO)_4Cr{\equiv}CPh}$ and $\mathrm{Br(CO)_4Cr{\equiv}CPhMe}$ obtained a mixture of tolane, phenyl-p-tolylacetylene and diparatolylacetylene [27].

R. R. Schrock synthesized first the high oxidation state neopentylidyne tungsten carbyne $\mathrm{Np_3W{\equiv}CtBu}$, which was found inefficient for alkyne metathesis [28]. Several other neopentylidyne complexes were then prepared, some of them giving rise to a stoichiometric reaction with diphenylacetylene, leading to the production of the initial metathesis product

PhC≡CtBu [29]. Interestingly, the (DME)Cl_3W≡CtBu reacted with 1 equivalent of hex-3-yne or but-2-yne to produce a stable metallacyclobutadiene, well characterized by X-Ray spectroscopy. Again, this complex was found inactive for alkyne metathesis: the first well-defined catalyst has been the trisalkoxy $(tBuO)_3W$≡CtBu complex, which transformed hept-3-yne with rates as high as 5 s^{-1} at 25°C [29].

Following this result, other trisalkoxy or phenoxy tungstacarbynes were synthesized: none of them were as reactive as the former t-butoxy one, but remarkably, the sterically hindered $[2,6-(iPr)_2C_6H_3O]_3W$≡CtBu led to the synthesis of well defined metallacyclobutadiene complex upon reaction with a dialkylsubstituted alkyne such as oct-4-yne. This complex was found to be active in metathesis and therefore considered as an intermediate for this reaction (scheme 8).



Scheme 8. Synthesis of a metathesis active tungstacyclobutadiene catalyst [29]

Other metallacyclobutadienes bearing fluorinated alkoxy ligands have also been prepared and behave similarly [30].

Some analogous molybdenum complexes have been synthesized in a similar way, and some of them have been also shown to catalyze alkyne metathesis, especially when using sterically hindered fluorosubstituted alcoxy or aryloxy ligands [31].

The results obtained by Moore almost 18 years later, using an in-situ procedure for the synthesis of sterically hindered phenoxymolybdenum carbynes (*vide supra*), are typically in line with this pioneering work.

Rhenium(VII) monoimido alkylidyne R'C≡Re(NAr)$(OR)_2$ complexes have also been shown to be active alkyne metathesis catalysts, but only with disubstituted acetylenes containing bulky groups, and with complexes that contains $OC(CF_3)_2Me$ withdrawing ligands [32].

4. Metathesis of monosubstituted alkynes.

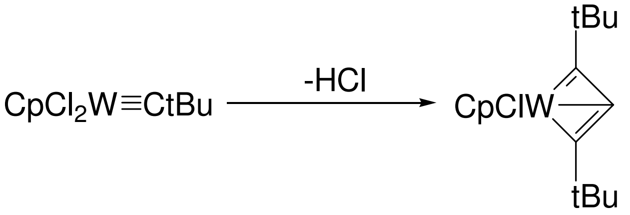
As already mentioned at the beginning of this paper, the use of WO_3-SiO_2 heterogeneous catalysts in attempts at metathesis of pent-1-yne only lead to aromatic trimers [3]. However, one may also find in the literature a paper related to the metathesis of terminal alkynes over CoO-MoO_3-SiO_2 catalysts (eqn 11) [4].

$$2\ \mathrm{Pr}{-}{\equiv}{-}\mathrm{H} \xrightarrow{\mathrm{CoO\text{-}MoO_3\text{-}SiO_2}} \mathrm{Pr}{-}{\equiv}{-}\mathrm{Pr} + \mathrm{H}{-}{\equiv}{-}\mathrm{H} \qquad (11)$$

As far as the homogeneous counterpart is con]}cerned, only few papers are dealing with this chemistry.

The interest of such a reaction would be evident in terms of applications, as the equilibrium would be displaced due to the release of acetylene, which furthermore could be reused for the synthesis of the starting material if necessary.

Attempts at this reaction were made by Schrock using the $CpCl_2W{\equiv}CtBu$ carbyne complex and tertiobutylacetylene: the initial reaction was indeed the formation of a metallacyclobutadiene intermediate, but the result was the production of a deprotiometallacyclobutadiene intermediate obtained via removal of HCl (eqn 12).

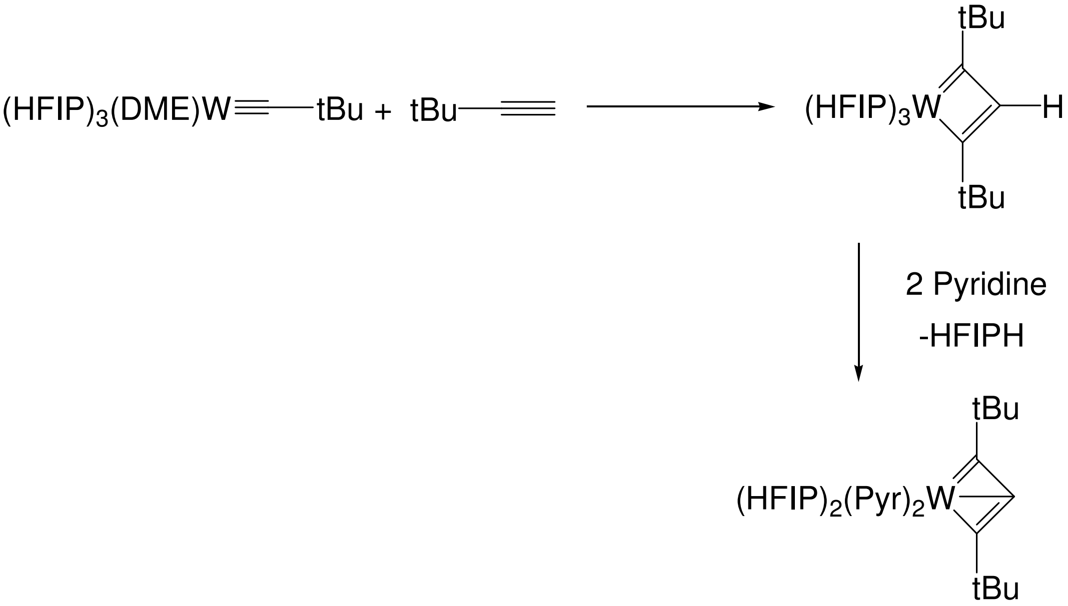


(12)

The same reaction conducted on phenylacetylene with the tris-tertiobutoxyphenyl carbyne complex $(tBuO)_3W{\equiv}CPh$ which can be used as catalyst for internal alkyne metathesis gave rise to similar results in the presence of pyridine (eqn 13).

$$(\mathrm{tBuO})_3\mathrm{W}{\equiv}{-}\mathrm{Ph} + \mathrm{Ph}{-}{\equiv} \xrightarrow[\mathrm{-tBuOH}]{\mathrm{2\ Pyridine}} (\mathrm{tBuO})_2(\mathrm{Py})_2\mathrm{W}(\mathrm{C}_3\mathrm{Ph}_2) \qquad (13)$$

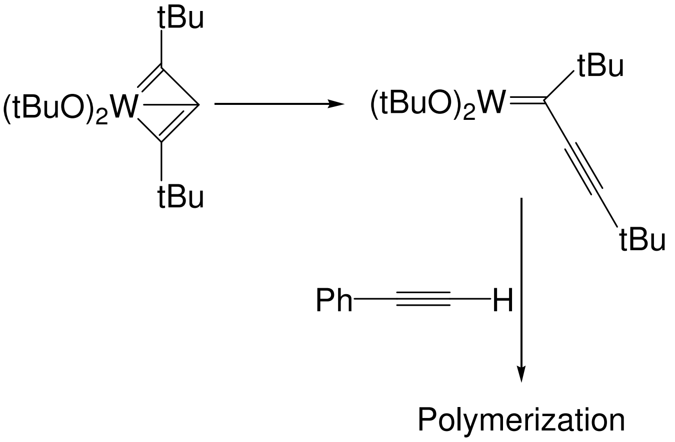
The fact that metallacyclobutadiene are intermediates in this reaction have been ascertained by a sequential reaction implying the $(HFIP)_3W{\equiv}CtBu$ complex (HFIP=hexafluoroisopropoxy) and tertiobutylacetylene, where the protonated metallacycle could be isolated, and further deprotonated in the presence of pyridine (scheme 9) [33].



Scheme 9: synthesis of well defined deprotiometallacyclobutadiene [33].

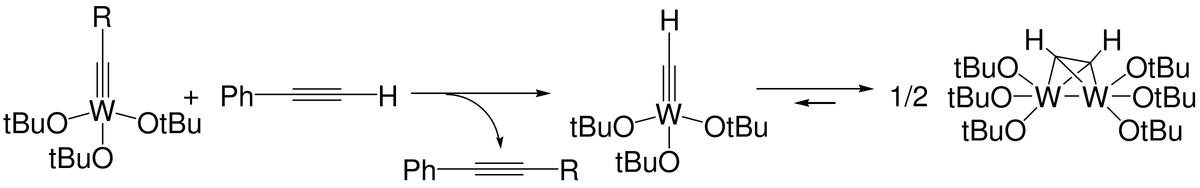
NMR studies have shown that the co-existence of both protonated and deprotonated species could occur, and that the equilibrium was shifted to the deprotonated species upon pyridine addition.

These deprotonated metallacycles are highly active catalysts for terminal alkynes polymerization as they are prone to be transformed into metallacarbenes (scheme 10) [34].



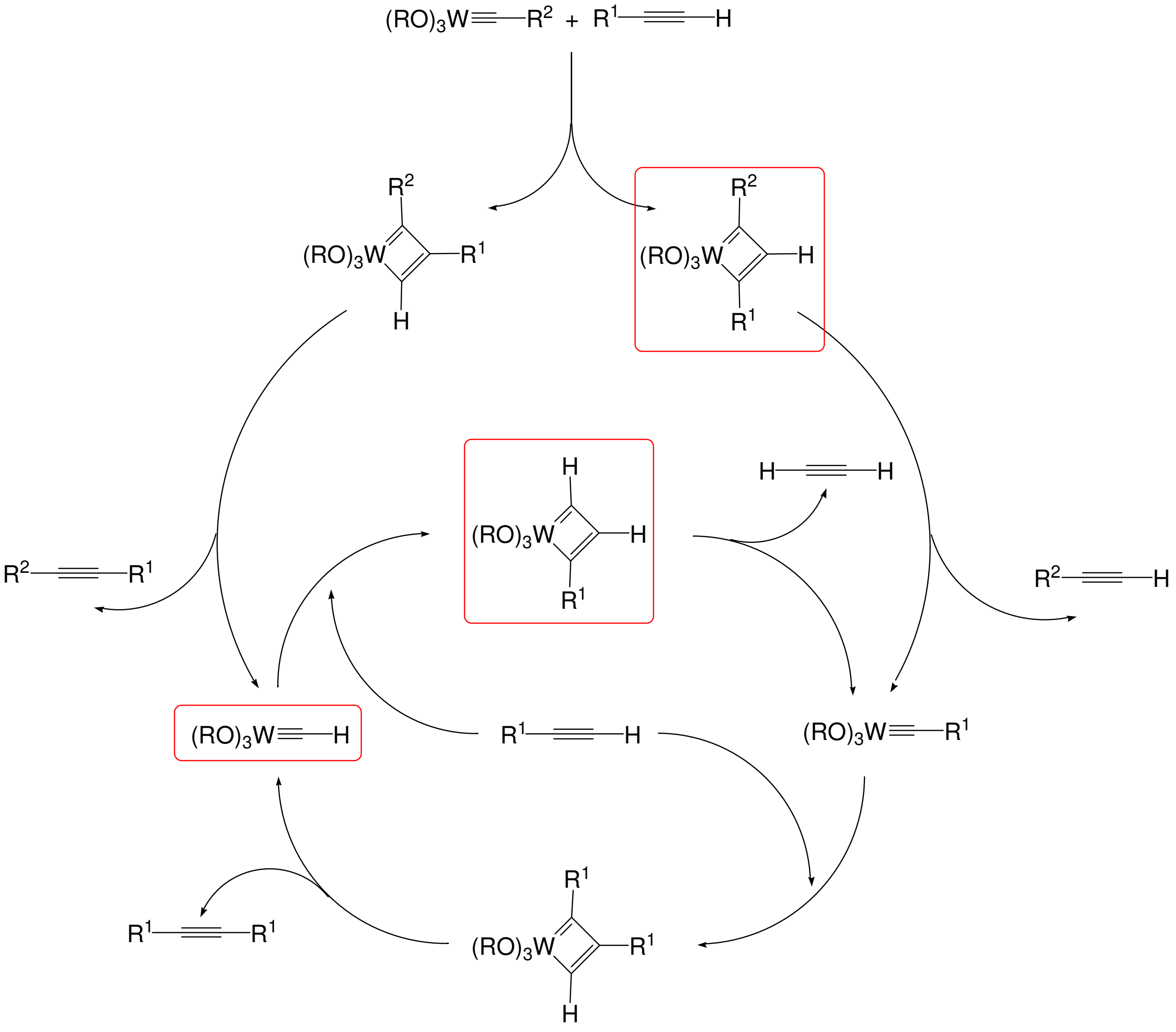
Scheme 10: Polymerization of phenylacetylene over deprotonated metallacyclobutadiene [34].

Another drawback which would be responsible for the lack of catalytic turnover has been suggested by Schrock, which relies on the formation of too stable dinuclear complexes formed via dimerization of the incipient methylidyne carbynes initially formed during the first step of the reaction (eqn 14):



(14)

This dimerization equilibrium had already been shown to occur in the presence of pyridine by Chisholm [35]. A general mechanistic scheme related to this chemistry is given below (scheme 10).



Scheme 11: catalytic cycle of terminal alkyne metathesis with drawbacks framed in red.

In 1993 however, attempts at homogeneous metathesis of terminal alkynes haves been successful, on the well defined $(tBuO)_3W\equiv CtBu$ complex [34]. The use of alkyl monosubstituted alkynes rather than aryl ones led to several turnovers in metathesis at room temperature, which were increased at high temperature (80°C) and upon using diethyl ether as solvent.

Nevertheless, the reaction course shifted rapidly to polymerization after the initial almost totally selective metathesis process. We recently revisited this reaction: considering that a coordinating solvent was able to stabilize the metathesis catalytic species, two different strategies were applied: The first one implied the use of an extra ligand in the coordination sphere of the Schrock carbyne complex $(tBuO)_3W{\equiv}CtBu$. In that context, the use of quinuclidine led to interesting results: 80% metathesis compounds were obtained at 80°C within 1 minute using 4 mol % catalyst during hept-1-yne metathesis. NMR studies on that reaction revealed the presence of methylidyne carbyne species, as well as the other alkylidyne propagating species, both stabilized by the quinuclidine ligand. In the same way, new sterically hindered hemilabile alkoxy-ether ligands were used, that could mimic the use of a bulky substituted group combined with the presence of an ether potentially coordinating function: this new complex was found to be not only as selective as the $(tBuO)_3W{\equiv}CtBu$-quinuclidine combination for hept-1-yne, but also gave a few turnover on phenylacetylene metathesis [36].

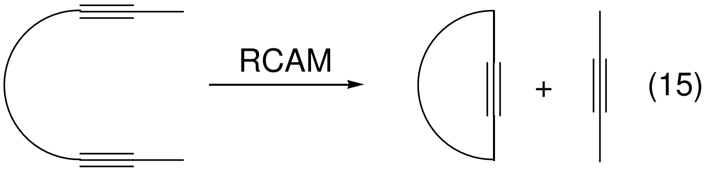
5. Applications

The application of alkyne metathesis is impeded by the availability and activity of the catalysts. The most convenient ones are with no doubt the molybdenum carbonyl-ArOH catalysts, for which improvement may be made via the use of different phenolic compounds, or using activation procedures involving either the use of a sacrificial alkyne [37] or that of an ether to reduce the activation temperature [20].

Although these catalysts are not yet well characterized, they don’t necessary need high reaction temperature – as stated by several authors – and may be successfully used at room temperature, via UV activation and can be used with functional alkynes.

The $O_2Mo(acac)_2$-$AlEt_3$-ArOH catalysts are probably less functional group tolerant, but are the most active ones reported in the literature, and compares well with the Schrock carbyne $(tBuO)_3W{\equiv}CtBu$ complex in terms of availability.

As far as the metathesis of functionalized alkynes is concerned, a systematic study of the use of different trialkoxymolybdenum (VI) alkylidyne complexes obtained in situ via the use of a trisamidomolybdenum (VI) propylidyne complex have shown that alkyl-aromatic alkynes bearing functional groups in a para position (CN, CF_3, CHO, OCH_3, $N(CH_3)_2$) could be metathesize under smooth conditions (30°C) generally using 10 mol % catalyst and 20h reaction time. The reactivity was strongly dependant on the phenoxy group structure, as it was the case for molybdenum carbonyl-ArOH systems: in that context, it has been reported that the use of 4-chlorophenol as a cocatalyst with $Mo(CO)_6$ enhanced the activity as well as for the use of 2-fluorophenol. This has been largely exemplified via the synthesis of several symmetrical diaryl substituted alkynes via the use of the $Mo(CO)_6$-ArOH combination with 5 to 10 mol % catalyst at 140°C for several hours [38], or cyclic alkynes via ring closure metathesis of diynes: cyclic lactones and lactames could be synthesized under the same conditions (eqn 15) [39]. Such a reaction allows obtaining at will the Z or E stereochemistry of the double bond by further control of the hydrogenation of the triple bond. In that context, Fürstner has applied his trisamidomolybdenum complex as a catalyst precursor for the synthesis of several natural products and the reader will find most of his results in a recent review [40].



Conjugated poly(para-phenylenethylenes) (eqn 10) are of potential interest for their optoelectronic properties: the use of diynes as substrates and the instant $Mo(CO)_6$-ArOH catalysts have also allowed the synthesis of a large variety of such polymers, the driving force of the reaction being the use of methylsubstituted alkynes, allowing to produce volatile but-2-yne.

Such reactions have been mostly studied by Bunz and his group, and have been the subject of a review [41].

6. Conclusion

This account devoted to alkyne metathesis catalysts shows how this reaction, for which the former catalysts have been found during the seventies-eighties, has got a renewed interest by the end of the nineties. Typically, this reaction has followed the same trend as olefin metathesis, the driving force being the use and improvements of the former catalysts for their application in metathesis of either functionalized alkynes for the synthesis of biologically active compounds, or in polymerization. Methyl-substituted acetylenes have been in most cases systematically used to complete these reactions via but-2-yne release under vacuum

The last results found using terminal acetylenes may give the opportunity to act in the same way via the formation of the more volatile ethyne, which would also be of interest from the atom economy concept. Improvement however need to be done in that field when aromatic monosubstituted alkynes are concerned, and may be the subject of further research in the molecular design of more selective catalysts for that reaction.

Attempts at increasing activities and functionality tolerance for disubstituted alkynes have led to improvements of the in situ Mo^0/ ArOH catalytic systems: the availability of Mo^0 complexes and that of different phenolic reagents, where a fine tuning of the electronic and steric properties could be easily made, should allow the discovery of new, more active and functionality tolerant Mo/ArOH couples for their application in synthesis.

Although the heterogeneous $Mo(CO)_6/SiO_2$ catalysts have been much less studied , they have been found to be active in a liquid phase. This system may be suitable to avoid the use of phenolic reagent in excess and be a starting point for further research in this field, via grafting molybdenum species on silica, a procedure which would be of particular interest from an environmental point of view.

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ABSTRACT

This paper presents the evolution of alkyne metathesis since the early discoveries , essentially from the catalyst point of view. It is shown that although well defined carbynes may be useful for this reaction, further work has been made, aimed at the synthesis of new catalysts or catalytic systems, based on molybdenum precursors , associated or not with phenolic co-catalysts. The major objectives have been to obtain more functional groups tolerants catalysts, for their application in organic synthesis, including RCM for further stereoselective hydrogenation of the triple bond in the cycle, as well as for polymerization of aromatic diynes.

Some insights into the possible mechanisms are given, and data relevant to the metathesis of

terminal alkynes, a still challenging reaction where polymerization is occurring via the formation of deprotonated metallacyclobutadiene, are also presented and discussed.