Advances and Challenges in User-friendly Alkyne Metathesis Catalysts

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Abstract:

Alkyne metathesis, the cousin of the “noble” alkene metathesis, has attracted rapidly growing attention within the past twenty years and has been widely used in the synthesis of natural products, functional polymers, and shape-persistent molecular architectures. Given some excellent reviews in recent years, this article will not provide a comprehensive review of the catalyst development and the wide applications of alkyne metathesis, but rather will focus on the rational design of the catalysts, substrate structures, and reaction conditions that meet the requirements of certain metathesis pathways (e.g., cyclooligomerization, polymerization, self-correction, etc.) and will make the catalytic systems more user-friendly and practically useful (e.g., operating in air, long lifetime, with broad substrate scope).

Introduction of alkyne metathesis

Since its early discovery in 1956, alkene **metathesis** (see Glossary) has widely been used in organic synthesis, polymer chemistry, and materials science [1,2]. It has become one of the most powerful transformations in modern organic chemistry. By contrast, **alkyne metathesis**, the cousin of the 'noble' alkene metathesis, has attracted growing attention only within the past twenty years or so given its great synthetic potential [3,4]. With the emergence of rationally designed catalysts with high activity, high stability and good functional group tolerance, alkyne metathesis has been widely used in the synthesis of natural products [5-7], functional polymers [8-11], and shape-persistent molecular architectures [12-15].

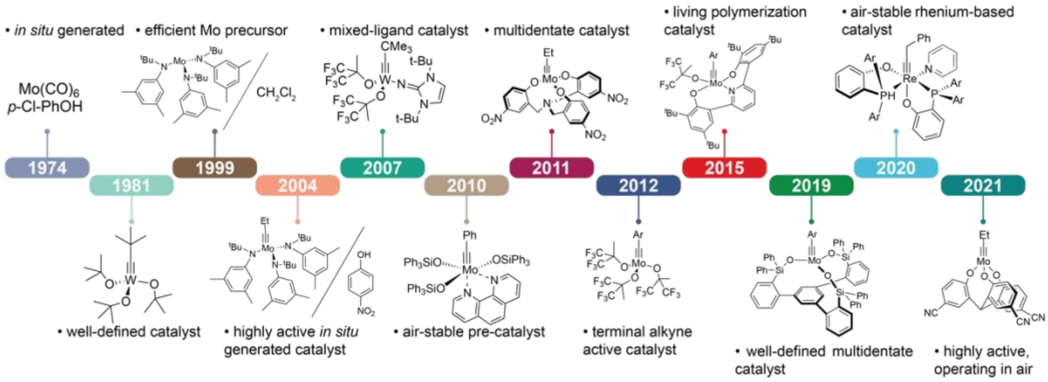


Figure 1. Representative homogeneous alkyne metathesis catalysts.

Alkyne metathesis catalyst development

Alkyne metathesis was first observed by Penella and co-workers in 1960s [16]. In 1974, Mortreux and co-worker discovered upon heating the mixture of $Mo(CO)_6$/phenols generated a homogeneous catalytic species that could catalyze alkyne metathesis (Figure 1) [17]. However, the required harsh condition (140 °C, 12h), poor functional group tolerance as well as the unclear mechanism impeded their wide applications [18,19]. Later, the well-defined tungsten **alkylidyne** catalyst [*t*-BuC≡W(O*t*-Bu)$_3$)] developed by Schrock [20] in 1981 enhanced the catalyst functional group tolerance, but its appreciable Lewis acidity made this complex incompatible with substrates containing heteroatoms such as nitrogen heterocycles, divalent sulfur, polyether chains or carbonyl-containing substrates, like ketones and aldehydes.

Based on Cummins' trisamidomolybdenum complex [21], in 1999, Fürstner et al. demonstrated that the combination of the Mo[N(*t*-Bu)(Ar)]$_3$ and CH_2Cl_2 could generate a catalytically active species for alkyne metathesis [22]. Later in 2004, Moore et al. made a significant improvement on this system to produce the metal alkylidyne species via a reductive recycle strategy almost quantitatively [23,24]. These complexes were used as precursors to prepare more efficient phenoxide based molybdenum alkylidyne catalysts. Notably, in 2010, Fürstner reported an air stable pre-catalyst whose catalytic activity was conveniently restored upon exposure to $MnCl_2$ showing outstanding functional group tolerance [25]. In 2012, the Tamm group [26] synthesized the complex [$MesC{\equiv}Mo(OC(CF_3)_2Me)_3$] that promoted not only the efficient metathesis of a wide variety of terminal alkynes, but also the unprecedented terminal ring-closing alkyne metathesis (TRCAM), though similar complexes had been reported by Schrock in 1984 without such applications demonstrated [27]. Almost at the same time, they reported the diyne cross metathesis (DYCM) and ring-closing diyne metathesis (RCDM) enabled by the catalyst [$PhC{\equiv}W\{OSi(Ot\text{-}Bu)_3\}_3$], affording unexpected diynes [28].

In 2011, Zhang and co-workers pioneered the synthesis of a series of multidentate organic ligands and the *in situ* generated molybdenum alkylidyne catalysts exhibited high catalytic activity, excellent functional group tolerance, fast reaction rate, and high stability [29,30]. Similarly, in 2019, the Fürstner group [31] and the Lee group [32] independently designed and synthesized well-defined multidentate catalysts based on tripodal silanolate ligands. Better functional group tolerance was observed compared with the previously reported catalyst containing monodentate triarylsilanolate ligand despite its lower activity and slower rates [33]. The failure in metathesis of electron-poor substrates (e.g., containing nitro, aldehyde group) is still the limitation of this type of catalysts. In 2021, the Zhang group reported a class of multidentate catalysts containing simple tris(2-hydroxyphenyl) methane ligands, which can advantageously operate in open air, while providing similar yields to those obtained under argon [34].

In 2020, alkyne metathesis mediated by a well-defined d^2 Re(V) alkylidyne complex was reported by the Jia group [35]. This catalyst was remarkably stable in both air and moisture and could catalyze the alkyne metathesis with a broad substrate scope, including alcohols, amines, and even carboxylic acids. Such d^2 Re(V) alkylidyne catalyst provided an alternative route toward the development of user-friendly alkyne metathesis catalysts.

Given some excellent reviews in recent years [3,4,36-43], this article will focus on the rational design of the catalysts, substrate structures, reaction conditions and more user-friendly and practically useful catalytic systems.

General catalyst formation

For most of the reported active alkyne catalysts, they generally involve a catalyst generation step, in which the metal alkylidyne precursor and selected ligand are mixed together to generate the active catalyst. The ligands would substitute the leaving group on precursor and chelate to the metal center to form the active alkyne metathesis catalyst (Figure 2). Since the catalysts are generally prepared from two components, metal alkylidyne precursors and organic ligands, we summarized some representative precursors and ligands in Figure 2 and will discuss those components respectively in this section.

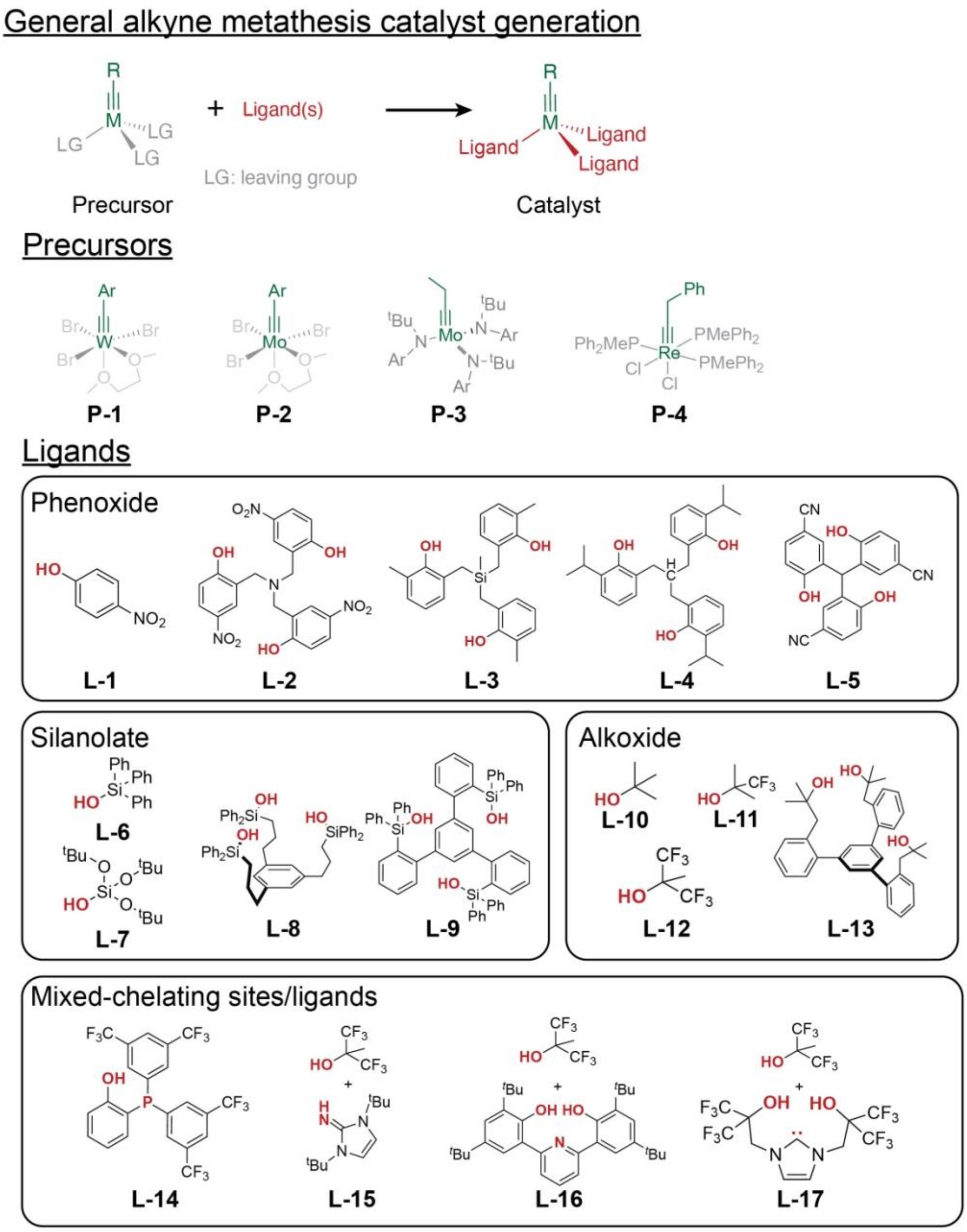


Figure 2. Representative alkyne metathesis catalysts, including metal alkylidyne precursors and organic ligands.

Metal alkylidyne precursors

The commonly used alkyne metathesis catalysts are mainly based on tungsten and molybdenum alkylidyne complexes. Besides the molybdenum and tungsten based catalysts, less reported rhenium complexes also showed activity in the metathesis of 5-undecyne [44]. There are mainly two types of precursors for the preparation of Mo and W based catalysts. One type is $[ArC\equiv M(Br)_3(dme)]$ (Figure 2, **P-1** and **P-2**). Since the previous precursor [$Me_3CC{\equiv}W(Cl)_3(dme)$] (dme = 1,2-dimethoxyethane) prepared by Schrock et al. via the "high-oxidation-state" route lacks variability in the alkylidyne fragment [27], the complexes **P-1** and **P-2** developed later *via* the "low-oxidation-state" route have been the dominant precursors [45-49], though less investigated precursors [$W_2(NMe_2)_6$], [$W_2(OR)_6$] and [$RC{\equiv}W(NMe_2)_3$] have been reported recently [50,51]. The other type is [$CH_3CH_2C{\equiv}Mo\{N(t\text{-Bu})(Ar)\}_3$] (Figure 2, **P-3**) that could react with the ligands to generate the active catalysts *in situ* through amide ligand substitution [52-54]. Additionally, $PhCH_2C{\equiv}ReCl_2(PMePh_2)_3$ (Figure 2, **P-4**) was recently explored as a precursor for rhenium based catalysts [35].

Organic ligands

Phenoxide

Phenoxide ligands (Figure 2, **L-1**) were commonly used in the molybdenum based catalysts. These catalysts were generated *in situ* from the above mentioned precursor **P-3** (Figure 2) that was prepared through a significantly improved reductive recycle strategy based on Fürstner's $Mo[N(t\text{-Bu})(Ar)]_3$ / CH_2Cl_2 system [23,24]. These catalysts exhibit high activity at room temperature and are compatible with a variety of functional groups.

Endeavoring to improve both the metathesis catalytic activity and functional group tolerance and shut down the undesired polymerization pathway, the Zhang group first introduced the multidentate ligands (Figure 2, **L-2**, **L-3** and **L-4**) into the catalyst design to purposely block one open substrate coordination site (inhibiting the undesired "ring-expansion" pathway) [29]. Satisfactorily, the multidentate catalyst exhibited high catalytic activity, significantly enhanced functional group tolerance, prolonged lifetime, and complete shutdown of the undesired polymerization of the 2-butyne by-product (catalyst poisoning), which has been a long-standing problem in alkyne metathesis.

Until now, alkyne metathesis catalysts that can operate under user-friendly open air conditions have always been hard to come by. Based on their previous success in the development of the trisphenoxide-based catalysts [29,52-54], very recently, the Zhang group reported a class of multidentate catalysts containing simple tris(2-hydroxyphenyl) methane ligands (Figure 2, **L-5**) [34], which can advantageously operate in open air, while providing similar yields to those reactions conducted under argon.

Silanolate

In 2009, triphenylsilanolate ligands (Figure 2, **L-6**) were developed for molybdenum complexes by Fürstner and co-workers [55], and the resulting catalyst showed high activity and outstanding functional group tolerance. Coordination of these species with 1,10-phenanthroline gives access to air-stable pre-catalysts [25], however, the lack of functionalizable sites in the catalyst structure impedes further tuning of their activity.

The Tamm group reported the tri(*tert*-butoxy)silanolate ligand (Figure 2, **L-7**) for tungsten benzylidyne complex in 2011 [56]. The corresponding catalyst proved the capability of silanolate-supported tungsten alkylidyne complexes in promoting the efficient metathesis of alkynes.

Inspired by the above multidentate catalyst study, the Fürstner group designed and synthesized tris-silanolate based multidentate catalysts (Figure 2, **L-8**) [57]. These *in situ* generated catalysts excelled in reactions of alkynes bearing primary, secondary or phenolic -OH groups, as well as in reactions of (bis)propargylic alcohol derivatives.

In 2019, the Fürstner group and the Lee group independently reported the new well-defined catalyst (Figure 2, **L-9**) [31,32]. The functional group tolerance was improved despite its lower activity. However, metathesis of electron-poor substrates (e.g., containing nitro group) still remains a challenge for this type of catalysts. Subsequently, comprehensive studies of this new family of canopy catalysts revealed that the chelate effect entailed even certain stability toward water [33]. These findings marked a big leap forward in alkyne metathesis.

Alkoxide

Alkoxide ligands, such as *tert*-butoxide (Figure 2, **L-10**) [58] or ligands with the combination of electron-withdrawing alkoxides (e.g., fluoro-*tert*-butoxide, Figure 2, **L-11**, **L-12**) and strongly electron-donating imidazolin-2-iminato (Figure 2, **L-15**) or related *N*-donor ligands [59-61], were used in the tungsten alkylidyne complexes. Those air- and moisture-sensitive catalysts can enable alkyne metathesis even at room temperature. However, their low functional group tolerance limited their applicability due to the Lewis acidity.

Very recently, the multidentate ligand **L-13** and corresponding W-based catalyst (Figure 2) was designed and synthesized [45]. Although this catalyst does not yet rival the best molybdenum alkylidynes known to date, it constitutes a new lead in the tungsten series.

Mixed-chelating sites/ligands

In 2020, the Jia group reported well-defined d^2 Re (V) alkylidyne complexes based on ligand **L-14** (Figure 2) [35]. This complex can catalyze alkyne metathesis with a broad substrate scope and it exhibits high stability under both air and moisture.

Recently, highly active catalysts bearing NHCs ligands **L-16** and **L-17** (Figure 2) for various olefin metathesis reactions [62,63] inspired the introduction of NHC ligands into alkyne metathesis catalysts [64-68]. But they still have much room for further improvement in activity.

Mechanism

Although new mechanisms were proposed in 2020 [69-71], the initial mechanism proposed by Katz in 1975 is still the widely accepted one, in which alkyne metathesis proceeds via square-pyramidal metallacyclobutadiene (MCBD) intermediates formed by [2+2] cycloaddition of the metal alkylidyne and an alkyne, followed by isomerization and cycloreversion [72].

These mechanism studies unraveled the relationship of the catalyst structure and activity and laid an important theoretical foundation for the design and synthesis of next-generation catalysts in the future.

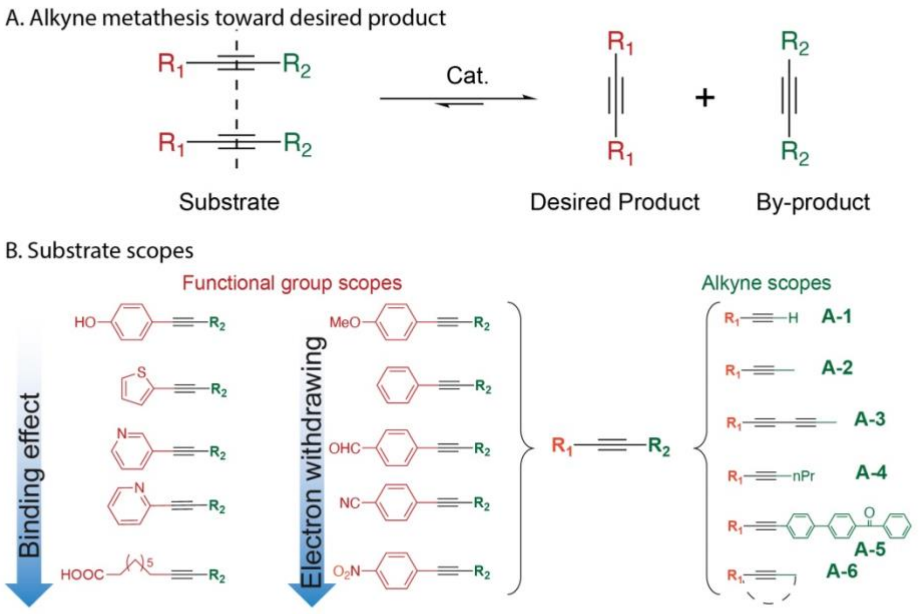


Figure 3. (A) alkyne metathesis productive pathway and (B) summary of substrate scopes.

Substrate scope

In order to realize the wide application of alkyne metathesis in organic synthesis, polymer chemistry and materials science, access to the desired products with various functional groups (Table 1) is important, and the 'leaving' group for the by-product formation should also be carefully designed (Figure 3).

Functional group scopes

The initial Mortreux's type catalysts showed a somewhat limited scope of functional group tolerance. Specifically, nitro, aldehyde-carrying substituent or heterocyclic aryl alkynes turned out to be incompatible [73].

The well-defined catalyst [*t*-BuC≡W(O*t*-Bu)$_3$)] developed by Schrock improved the group tolerance, but this complex was incompatible with substrates containing heteroatoms such as nitrogen heterocycles, divalent sulfur, or polyether chains due to their appreciable Lewis acidity [27,74].

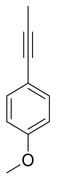
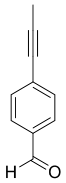
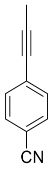
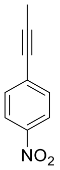
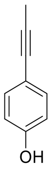
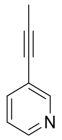
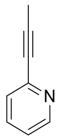
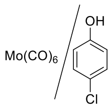
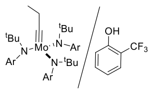
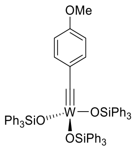
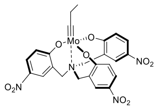
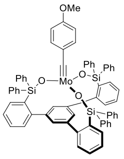
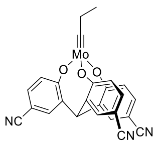
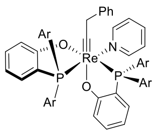
Two types of catalysts based on monodentate ligands were reported later. [PhC≡Mo(OSiPh)$_3$)] (Figure 2) reported by the Fürstner group in 2010 [25], was tolerant of most of the functional groups reported in alkynes except for aldehyde group. The other one, generated *in situ* from the precursor and *p*-nitrophenol, was developed by the Moore group [24] and exhibited excellent functional group tolerance including those challenging groups on aryl alkynes such as cyano and aldehyde (Figure 3B).

Currently, the representative catalysts with excellent functional group tolerance are based on multidentate ligands: the "canopy" catalyst reported by the Fürstner group [31,32] and the *in situ* generated catalyst based on multidentate phenoxide ligand reported by the Zhang group [34].

The compatibility of the well-defined "canopy" catalysts with various functional groups is outstanding. Whether electron donating groups such as ethers, silyl ethers, thioethers, amides, hydroxy and carbamates or electron withdrawing groups such as tosylate, esters, ketones, epoxides and trifluoromethyl groups are well tolerated. Moreover, aromatic heterocycles including pyridine, thiophene, thiazole, and carbazole can be metathesized without problems. However, attempts to metathesize a propynylated benzaldehyde and nitrobenzene derivative failed.

The *in situ* generated catalysts based on the multidentate phenoxide ligands (Figure 2) also showed excellent functional group tolerance as it is compatible with different substrates containing electron-donating/electron-withdrawing groups, heterocyclic molecules (pyridine, thiophene, and carbazole), and free phenolic hydroxy groups. Even those challenging substrates, containing nitro, cyano or aldehyde functional groups are compatible to give the corresponding dimers in excellent yield (89-96%) at 70 °C within 30 min (Table 1). Further development of these multidentate phenoxide based catalysts would involve catalyst structure elucidation using single-crystal X-ray diffraction and replacement of the required small amount of CCl_4 solvent with a more user-friendly one.

Table 1. Summary of the representative catalysts and their catalytic performance.

							
	72%; 140 °C; 12-16h	×[a]	15%; 140 °C; 12-16h	×	69%; 140 °C; 12-16h	×	/[b]
	83%; 30 °C; 22h	47%; 30 °C; 22h	37%; 30 °C; 22h	/	/	/	/
	97%; 80 °C; 30min	×	/	×	/	88%; 50 °C; 3h	/
	87%; rt; 4h	71%; 40 °C; 7h	/	55%; 40 °C; 12h	/	/	20%; 70 °C; 3h
	92%; rt; 9h	decomposition	77%; 60 °C; 12h	×	93%; 60 °C; 12h	62%; 90 °C; 12h	/
	98%; rt; 0.5h	96%; 70 °C; 20 min (95%, rt,3h)	89%; 70 °C; 30 min	89%; 70 °C; 30 min	98%; 70 °C; 20 min	/	40%; 70 °C; 30 min
	91%; 100 °C; 8h	95%; 100 °C; 16h	/	/	72%; 100 °C; 16h	/	/

[a]: no metathesis product was observed.

[b]: substrate was not reported in the paper.

Alkyne scopes (‘Leaving’ group of alkyne)

In the light of the rapid development of the catalysts, the structures of the alkyne substrates remain largely unexplored. Because of the reversible feature of alkyne metathesis, the structures of the alkyne, especially the “leaving” groups, should also be carefully designed to drive the reaction equilibrium toward the product formation.

Terminal alkyne

The alkyne metathesis remains largely limited to the use of internal alkynes, whereas the use of terminal alkynes (Figure 3B, **A-1**) are extremely rare because of the strongly competing substrate polymerization side reaction or deactivation of the catalysts by the byproduct ethyne. Hept-1-yne metathesis was realized by the Mortreux group in 2006 through addition of quinuclidine as an external ligand to the (*t*-BuO)$_3$W≡C(*t*-Bu) alkylidyne complex [75].

In 2012, the Tamm group [26] reported the complex [MesC≡Mo{OC(CF$_3$)$_2$Me}$_3$] (Figure 2), which fulfilled both the efficient metathesis of a wide variety of terminal alkynes and the unprecedented terminal ring-closing alkyne metathesis (TRAM).

The same group also reported the synthesis of tungsten complexes [Mes≡CW{OC(CF$_3$)Me$_2$}$_3$] (Figure 2) [46]. The results showed that the catalyst could catalyze the metathesis of both internal alkynes and terminal alkynes. Notably, it represents the first tungsten alkylidyne complex that is able to promote the metathesis of terminal alkynes in an efficient manner and also it is the first catalyst that can promote alkyne cross-metathesis (ACM) of two terminal alkynes efficiently, whereas several ACM reactions involve one terminal alkyne and one internal alkyne. The self-metathesis, ring-closing alkyne metathesis and cross-metathesis of terminal alkynes were also realized by ditungsten(III) complex W$_2${OC(CF$_3$)Me$_2$}$_6$ [50].

The Fürstner group utilized the commercially available complex [*p*-OMeC$_6$H$_4$C≡Mo(OSiPh$_3$)$_3$)] (Figure 2) as the catalyst and demonstrated the metathesis of terminal alkynes [76]. Subsequently, in 2014, they systematically studied the largely unknown cross-metathesis of terminal alkynes [77]. Gratifyingly, ACM of terminal alkyl alkynes with propynyl(trimethyl)silane worked well at ambient temperature in the presence of esters, carbamates, sulfonamides, aryl chloride or acetal moiety. ACM of the less reactive terminal aryl alkynes and internal alkynes RC≡CMe were surprisingly fast when the aryl alkyne contained one or more electron-withdrawing groups. For less electron-deficient aryl alkynes, rapid and quantitative polymerization was observed. A large excess (4 equiv) of the internal alkynes RC≡CMe was needed in order to obtain respectable cross metathesis results.

Methyl-capped alkyne or diyne

In the early studies, alkyne metatheses were performed in high-boiling-point solvents under vacuum-driven condition to remove the byproduct 2-butyne. As the boiling point of 2-butyne is only 27 °C and it can be adsorbed by molecular sieves (MS 5Å) [25], methyl-capped alkynes (Figure 3B, **A-2**) were usually selected for metathesis, and they are still the most commonly used substrates so far. It should be noted that for the Mo alkylidyne catalyst generated *in situ* from *p*-nitrophenol, metathesis of 2-propynylthiophene was unsuccessful while 69% conversion was achieved when 2-butynylthiophene was used as the starting material [24]. Subsequent studies revealed that the catalyst appeared to be poisoned after polymerizing 2-butyne and ethyl-capped alkynes (3-hexyne byproduct does not polymerize) were proven to be the most effective in metathesis. However, later when the newly developed multidentate ligand catalysts were utilized, the 2-butyne polymerization could be completely shut down [29], so the study of ethyl-capped alkynes has been stagnant since then.

It should be noted that methyl-capped conjugated diynes (Figure 3B, **A-3**) also went through the diyne cross metathesis (DYCM) and ring-closing diyne metathesis (RCDM) catalyzed by the tungsten alkylidyne complex [Ph≡CW{OSi(O*t*-Bu)$_3$}$_3$], affording unexpected diynes [28,78,79]. Interestingly, in 2020, the Trolez and Mauduit groups [80] obtained triynes using methyl-capped conjugated diyne in the presence of the well-known catalyst [*p*-OMeC$_6$H$_4$C≡Mo(OSiPh$_3$)$_3$)] (Figure 2), by introducing bulky groups into the starting materials. Less sterically-hindered Si-substituent such as trimethylsilyl (TMS), triethylsilyl (TES) or triphenylsilyl (TPS) groups would only give symmetrical diyne products which were consistent with the previous observations made by the Tamm group [28]. Very recently, the complex [MesC≡Mo{OC(CF$_3$)$_3$}$_2${OSi(O*t*-Bu)$_2$(OMes)}] also proved to be an excellent catalyst for the selective conversion of sterically encumbered methyl-capped conjugated diynes into symmetrical 1,3,5-triynes [48].

Propyl-capped alkynes

Compared with the inconvenient preparation of methyl-capped and ethyl-capped alkynes (1-propyne and 1-butyne gases are hard to handle quantitatively), propyl-capped alkynes (Figure 3B, **A-4**) could be easily prepared via Sonogashira coupling reaction between liquid 1-pentyne and different halogenated compounds. In 2020, Tilley and co-workers reported such an example in the synthesis of a shape-persistent aromatic macrocycle [81,82]. The byproduct, 4-octyne, could also be trapped by 5Å MS.

Benzoylbiphenyl-substituted alkynes

Before the usage of 5Å MS as the adsorbents for the byproduct 2-butyne [25], attempts to prepare shape-persistent macrocycles on gram scale using methyl capped alkynes resulted in poor yields, presumably due to the low efficiency in the byproduct removal. Therefore, the benzoylbiphenyl-substituted alkynes (Figure 3B, **A-5**) were selected for metathesis [83] and long rigid diarylethyne byproduct precipitated out the solution upon formation due to its extremely poor solubility. Therefore, byproduct removal via precipitation, rather than evaporation or adsorption, provided an efficient way to shift the metathesis equilibrium. The yield was nearly quantitative in spite of its low reaction atom-economy.

Ring-strained alkyne

Due to the lack of cyclic alkyne substrates, **ring-opening alkyne metathesis polymerization (ROAMP)** is still in its infancy [8,84-86]. ROAMP of cyclooctyne catalyzed by $[(t\text{-BuO})_3\text{Mo}{\equiv}\text{CPr}]$ was first reported by Schrock and coworkers in 1987 [87], with a broad molecular weight distribution (PDI > 4) was observed.

In 2019, the Fischer group [8] realized the ROAMP of ring-strained macrocylic dialkyne for the preparation of poly-(arylene ethynylene), a precursor for the synthesis of graphene nanoribbons (GNRs). This approach enabled access to GNRs with deterministic control over the ribbon length and end group functionality. It paved the way toward the rational synthesis of complex intraribbon GNR hetero-junctions from block copolymer templates.

Catalyst selectivity vs. reactivity

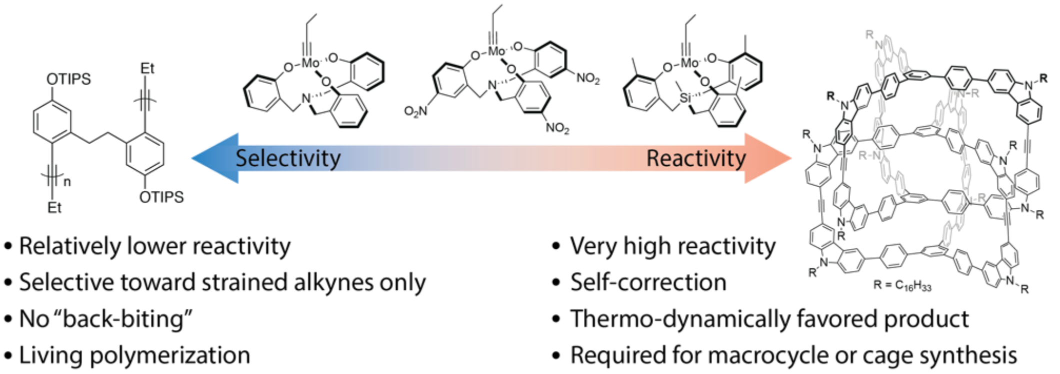


Figure 4. Different selectivity and reactivity of the alkyne metathesis catalysts needed for different targets.

As discussed above, with highly active catalysts, small molecule dimer products can be obtained in high yields. Generally speaking, the higher activity the catalysts have, the more efficient the self-correction is and the faster the reaction reaches equilibrium, and the more likely thermodynamically favored products are formed. In 2015, the predominant formation of the thermodynamically stable 3D molecular cage was achieved when the highly active catalyst was used, while only oligomers were obtained when a less active catalyst was applied [88].

On the other hand, with the decrease of the catalytic activity, the selectivity of the metathesis catalyst will generally be increased (Figure 4). For the synthesis of arylene ethynylene polymer via ROAMP, the catalyst with relatively lower activity would be a better option because an effective initiator should ideally only react with highly strained monomers but not catalyze cross-metathesis scrambling of the resulting polymer chains (back-biting). In 2013, Nuckolls and co-workers utilized a relatively less reactive catalyst, based on the multidentate Mo alkylidyne complex originally developed by the Zhang group, in ROAMP, and successfully realized the living polymerization of strained cyclooctyne with a PDI of 1.3 [84].

User-friendly catalytic system

Although the recently developed catalysts discussed above showed outstanding activity and broad substrate scope, most of them still suffer from the sensitivity toward air and moisture. The development of user-friendly catalytic system that doesn't require stringent air-free or moisture-free condition while retaining high activity and excellent group tolerance is highly desired. Three strategies have been established to resolve such issue.

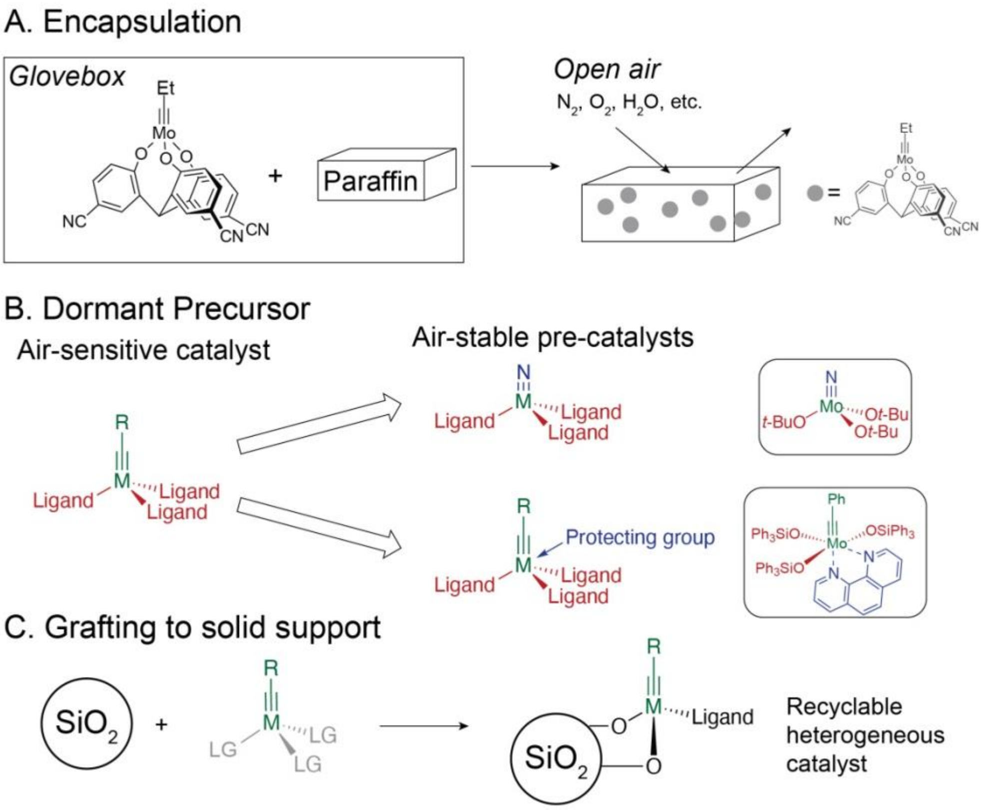


Figure 5. Strategies for promoting user friendliness and practical applications of the alkyne metathesis catalysts.

Encapsulation

To improve the user friendliness in handling and storage of the catalyst and make it easy to handle in air, the Zhang group explored the storage of the catalyst encapsulated in paraffin on benchtop under ambient condition [34]. The activated catalyst was dispersed in hot liquid paraffin wax, and the mixture was solidified gradually with stirring in the glove box (Figure 5A). The catalytic activity of the catalyst in open air remained the same after 24 h benchtop storage under ambient conditions. Gratifyingly, 53% yield was obtained even after the catalyst was stored in air for one month. When the catalyst loading was doubled (10 mol%), the one-month aged catalyst still provided 94% yield .

Dormant Precursor

In 2009, Fürstner and co-workers found that the pyridine coordinated catalyst [$N{\equiv}Mo(OSiPh_3)_3$)(Phen)] could function in dry air without compromising yield although high temperature and higher loading were necessary (Figure 5B) [55]. Shortly after this report, the Moore group activated this catalyst with a Lewis acid ($B(C_6F_5)_3$) weakening the Mo≡N bond and significantly enhanced the rate of metathesis [89] However, this precursor can still eventually hydrolyze and hence must be stored under an inert atmosphere. To address this issue, several other ligands and catalysts were tested. In 2010, the Fürstner group reported two 1,10-phenanthroline coordinated crystalline complexes ([$N{\equiv}Mo(OSiPh_3)_3$(Phen)] and [$PhC{\equiv}Mo(OSiPh_3)_3$(Phen)]), which were inactive but stable on the benchtop [25]. Gratifyingly, the catalytic activity could be restored upon treatment of the complex with $MnCl_2$, which formed stable complex with phenanthroline and opened up the Mo center.

Grafting to solid support

Grafting of the molecular catalysts onto dehydroxylated silica could also be considered as a useful user-friendly strategy [90-95] due to the easy isolation of the heterogeneous catalysts and their recycling.

Although silica-supported [$Mo(CO)_6$] or rhenium catalyst and alumina- or titania-supported molybdenum species have been reported, none of them were efficient. Considering that the pK_as of the phenol and silanol are similar, in 2006, Moore and co-workers reported the silica-supported heterogeneous catalyst which exhibited high activity, selectivity and good stability presumably due to the prevention of bimolecular deactivation [91]. Notably, the catalyst is recyclable and shows good activity over at least three cycles.

In 2016, the Tamm and Copéret groups grafted the known molecular catalyst [$MesC{\equiv}Mo(O^tBu_{F6})_3$] (Mes = 2,4,6-trimethylphenyl) onto partially dehydroxylated $SiO_{2\text{-}700}$ [94]. The supported catalyst showed unusually high TOFs (up to 2.3 s^{-1}) and TONs (up to 54 000). However, the supported catalyst is less reactive than the corresponding molecular complex, presumably due to the limited conformational freedom thus substrate accessibility to the surface species.

Concluding Remarks and Future Perspectives

The past two decades have witnessed tremendous progress in the field of alkyne metathesis, particularly since 2010, in both fundamentals and practical applications. Many well-defined catalysts have been widely used in the synthesis of natural products and materials. Inspired by the triphenolamine ligand based catalysts, various multidentate ligands have been used in preparation of several new active canopy catalysts. Particularly, very recently, the alkyne metathesis in open air condition has been realized. It has been demonstrated that Re catalysts can also catalyze alkyne metathesis reactions. Since W/Mo catalysts are generally sensitive to water, oxygen and certain (especially protic) functional groups, Re complexes represent promising candidates for novel catalyst development in the future.

Despite the impressive achievements so far, a number of challenges we are still facing today need to be overcome. We can now conduct the metathesis reaction in open air but the lifetime of the catalysts in the air is still relatively short. Development of a “dream” catalyst with robustness to air and moisture is still a challenging task in this field. It is also highly desired to design even shorter routes to known or new catalysts or precursors. Although the heterogeneous catalysts have been less studied, due to the ease of separation and recycling, this is still an important field full of potential, particularly from an environmental perspective. In contrast to disubstituted internal alkynes, metathesis of terminal alkynes, especially aromatic alkynes, has yet rarely been reported, which may be due to the known challenges in polymerization of the terminal alkynes or deactivation of the catalysts. Therefore, it is particularly important to develop efficient catalysts for terminal alkyne metathesis. Moreover, development of controlled alkyne metathesis that can be turned on and off under external stimuli would be highly useful for material synthesis. We believe that given a growing number of well-defined and/or highly active catalysts and emerging important applications, alkyne metathesis will be playing a more critical role in organic synthesis and materials development in the future.

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Declaration of interests

The authors declare no competing interests.

Glossary

Metathesis: Metathesis is a reaction in which two compounds exchange components with each other to form another two compounds with swapped components.

Alkyne metathesis (AM): Reaction involving reversible breaking and reformation of carbon-carbon triple bonds in alkynes.

Alkylidyne: Alkylidyne is an electrically neutral carbon active intermediate with three free electrons.

Ring-opening alkyne metathesis polymerization (ROAMP): Ring opening reaction of ring-strained alkynes to form alkyne polymer.

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