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Chapter 1

Silver Catalysis for Click Reaction

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1.1 Click Reaction:

If we peep through the nature's creation of life it can be seen that taking carbon dioxide as starting material the most of the reactions that are essential to sustain life are performed in water catalyzed by various enzymes; all designed for specific purpose.

Again, nature's inclination for making carbon-heteroatom bond over cabron-carbon bond is reflected well in the building blocks of life: Nucleic acids, proteins, and polysaccharides which are being stitched together from their smaller units (amino acids, glucose) through carbon-heteroatom bond.

Inspired by nature's brilliance, American chemist Dr. K. B. Sharpless addressed a terminology "click chemistry" to a set of reactions that are fast, simple, easy to purify, versatile, regiospecific, and high yielding for the rapid synthesis of useful new compounds and combinatorial libraries through heteroatom links (C-X-C) [1].

In chemical synthesis, "click" chemistry, more commonly called tagging, is a class of biocompatible reactions intended primarily to join substrates of choice with specific biomolecules. The concept of a "click" reaction has been used in pharmacological and various biomimetic applications. They have been made notably useful in the detection, localization and qualification of biomolecules.

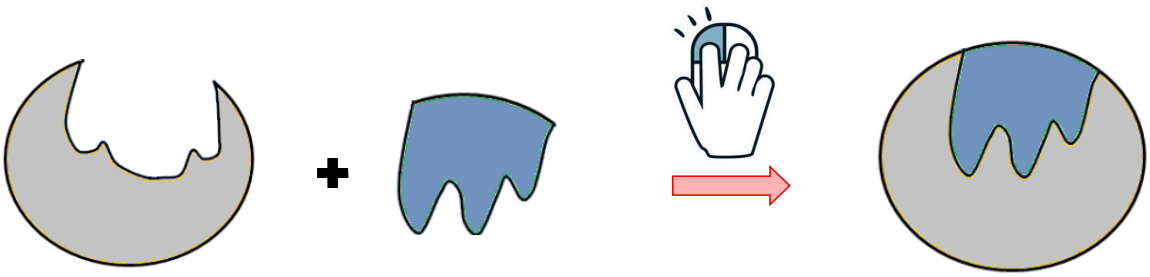


Figure 1.1: Schematic diagram showing how click reaction joins two molecules together

After its discovery, click reaction attain immense popularity among researchers working on various fields of chemistry and material science. Just to gain a brief idea about popularity of this particular reaction a statistical survey made by searching the keyword click reaction on Sci Finder shows that 2009 onwards more than 1000 research articles got published each year till date as depicted in **Figure 1.2**.

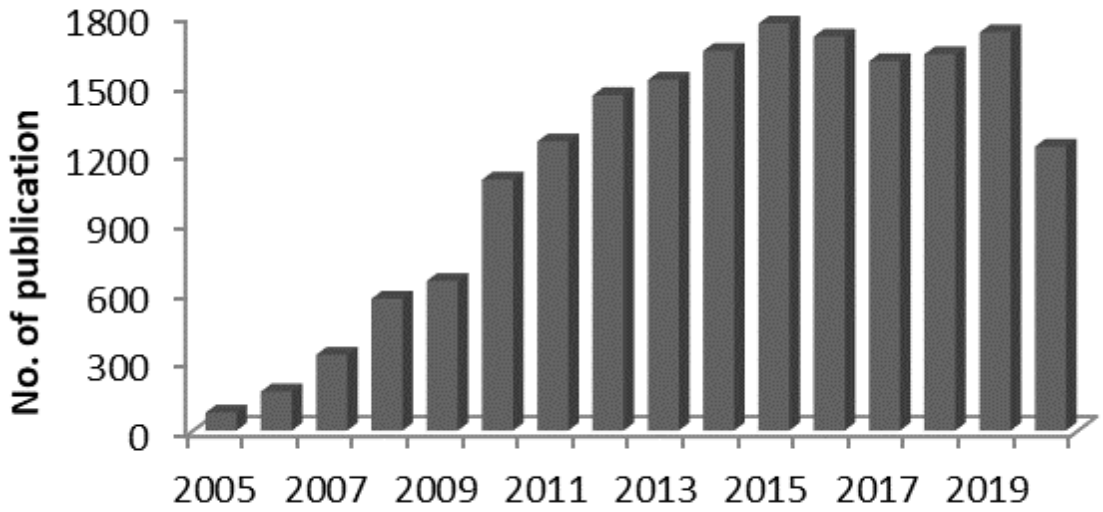


Figure 1.2: Statistical overview of click reaction related article published from 2005 till date

1.2 Classification of Click Reaction:

As mentioned earlier in the previous section click chemistry is not a single reaction but a group of many which follow certain criteria-simple to perform, have high yields, require no or minimal purification, and are versatile in joining diverse structures without the prerequisite of protection steps.

To date, four major classifications of click reactions have been identified.

- **Cycloadditions:** these primarily refer to 1, 3-dipolar cycloadditions, but also include hetero-Diels-Alder cycloadditions.
- **Nucleophilic Ring-Openings:** these refer to the openings of strained heterocyclic electrophiles, such as aziridines, epoxides, cyclic sulfates, aziridinium ions, episulfonium ions, etc.
- **Non-Aldol Carbonyl Chemistry:** this class of reaction include the formations of ureas, thioureas, hydrazones, oxime ethers, amides, aromatic heterocycles etc. Carbonyl reactions of the aldol type generally have low thermodynamic driving forces; hence they have longer reaction times and give side products, and therefore cannot be considered click reactions.
- **Additions to Carbon-Carbon Multiple Bonds:** examples include epoxidations, aziridinations, dihydroxylations, sulfenyl halide additions, nitrosyl halide additions, and certain Michael additions.

Various reactions falling under click reactions are shown in **Figure 1.3**

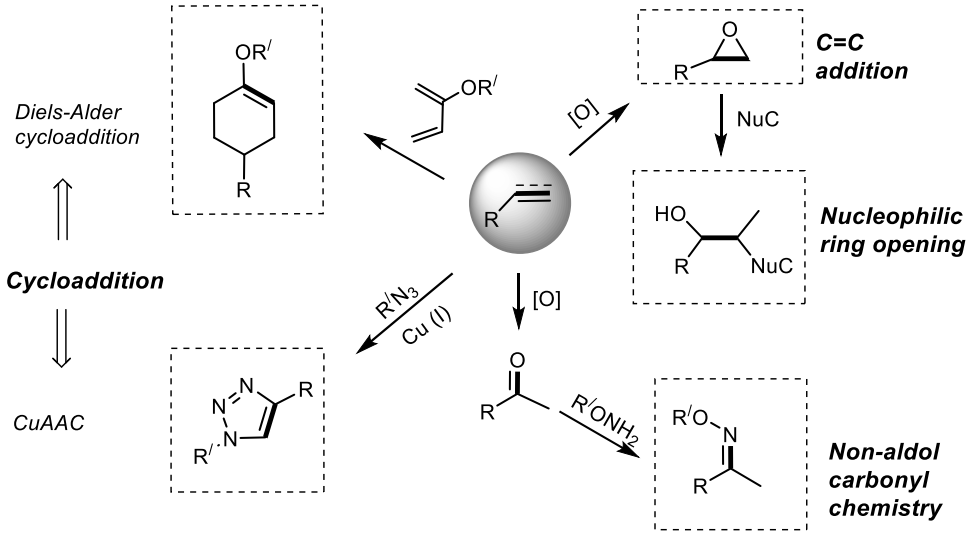
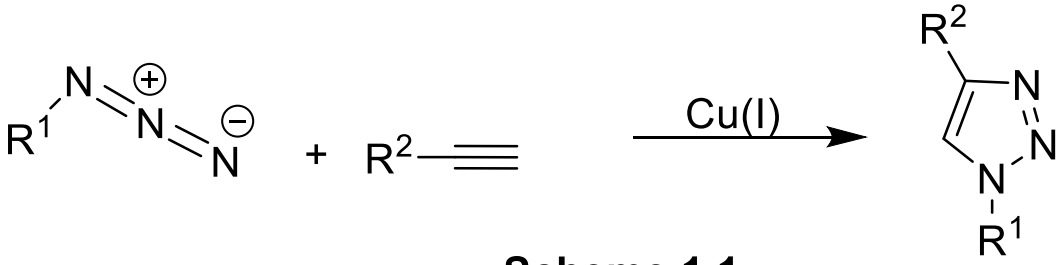


Figure 1.3: Various click reactions

Among the various click reactions the most studied example is the copper catalyzed azide-alkyne cycloadition (CuAAC) to form 1, 4-disubsituted-1, 2, 3-triazoles (Scheme 1.1). The copper (I)-catalyzed reaction is mild and very efficient, requires no protecting groups and purification in many cases [2, 3]. The azide and alkyne functional groups are largely inert towards biological molecules and aqueous environments, which allows the use of the CuAAC in target guided synthesis [4] and activity-based protein profiling [5].



Scheme 1.1

The triazole has similarities to the ubiquitous amide moiety found in nature, but unlike amides, is not susceptible to cleavage. Additionally, they are nearly impossible to oxidize or reduce.

The active Cu (I) catalyst can be generated from Cu (II) salts using sodium ascorbate as the reducing agent. Addition of a slight excess of sodium ascorbate prevents the formation of oxidative homocoupling products. Disproportionation of a Cu (II) salt in presence of a Cu wire can also be used to form active Cu (I) species [6-8]. However, use of Cu (II) source for CuAAC is problematic in biocojugation applications.

1.3 Mechanism of the Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC):

In general, cycloaddition reactions proceed via a concerted mechanism. However, experimental kinetic data [9] and molecular modeling performed on the CuAAC reaction predicts a stepwise reaction pathway. Several studies intending to investigate the mechanism of the CuAAC have been reported. These studies suggest involvement of polynuclear copper (I) intermediates in the mechanism and it is supported by theoretical studies [10].

Moreover, current development in 1, 3-dipolar cycloadditions of 1-halo- and 1-metalloalkynes with organic azides have driven additional investigation of the mechanism. In the case of 1-iodoalkynes, for the copper (I) - acetylide formation and cycloaddition to occur the terminal Csp-I bond need not to be broken, suggesting that the copper catalyst undergoes the cycloaddition purely via weak π-interactions with the internal alkyne.

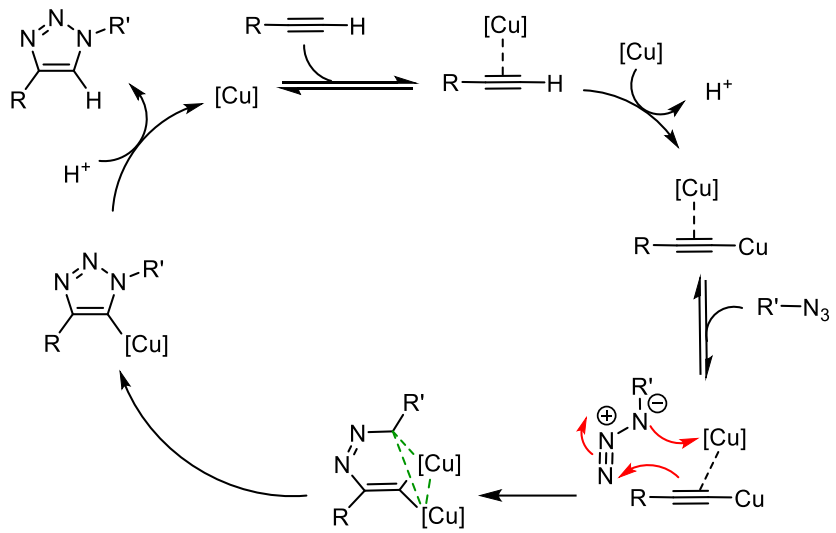


Figure 1.4: Catalytic cycle showing formation of 1, 4-disubstituted-1, 2, 3-triazole by CuAAC

DFT calculations have shown that coordination of Cu (I) to the alkyne is slightly endothermic in MeCN, but exothermic in water, which is in agreement with an observed rate acceleration in water. However, coordination of Cu to the acetylene does not accelerate a 1, 3-dipolar cycloaddition. Such a process has been calculated to be even less favorable than the uncatalyzed 1, 3-dipolar cycloaddition. Instead, a σ-bound copper acetylide bearing a π-bound copper coordinates the azide.

Then, an unusual six-membered copper metallacycle is formed. The 2nd copper atom acts as a stabilizing donor ligand. Ring contraction to a triazolyl-copper derivative is followed by protonolysis that delivers the triazole product and closes the catalytic cycle [11]. The overall mechanism for the CuAAC is shown in **Figure 1.4**.

Copper catalyzed click reaction is undeniably the fastest and convenient route to access 1, 2, 3-triazoles. However, use of copper may possess some serious threat of cytotoxicity [12]. Excess copper intake may also lead to neurological disorder, hepatitis, kidney damage, alzeheimer's disease etc. [13].

Moreover, copper (I) species may affect alkyne homocoupling or Glaser Hay coupling to form diacetylenes. Accordingly, copper free protocols that offer similar superiority of copper catalysts are always encouraged.

A search for copper free catalysts revealed many other transition metal catalysts (Ru, Rh, Zn, An, Ni, Pd and Ag) as well as organocatalysts can efficiently promote this reaction [14]. However, this chapter only deals with Ag catalyzed click reaction to furnish 1, 2, 3-triaoles.

1.4 Silver-An Overview:

Silver is placed in 11th group of periodic table, group of coinage metals and has an electronic configuration of $[Kr]4d^{10}5s^{1}$. Owing to the presence of half-filled 5s orbital, it can exist as either native metal, as an alloy with gold and other metals or silver (I) salts with a variety of counter anions. Silver is associated with the highest electrical and thermal conductivity, reflectivity, while lowest contact resistance known to any metal.

Generally silver salts are established as being good σ-/π-Lewis acids with stronger preference for σ-coordination over π-coordination. Stronger σ-coordination of silver is due to availability of vacant f-orbitals and relativistic contraction of electron cloud. Presence of fully filled 4d orbitals enables silver to establish favourable interactions with the carbon-carbon π-bond of alkynes (**Figure 1.5**). This property of silver (I) salts is known as alkynophilicity. Hence, silver (I) salts are recognized as being powerful catalysts in alkyne activation [15].

In addition to their ability to interact with π-systems to promote useful reactivity, the use of silver in organic transformations has important economic benefits relative to other more expensive transition metals such as gold, palladium and platinum. Review articles by Fang et al. [16] have discussed various Ag catalyzed

reaction of alkynes while Clarke et al. have published excellent review on Ag catalysts in indole synthesis [17].

Considering the ability of Ag to activate acetylenes, it is believed that it can also act as a potential catalyst for click reaction. In the next few sections of this chapter catalytic ability of Ag towards click reaction is discussed.

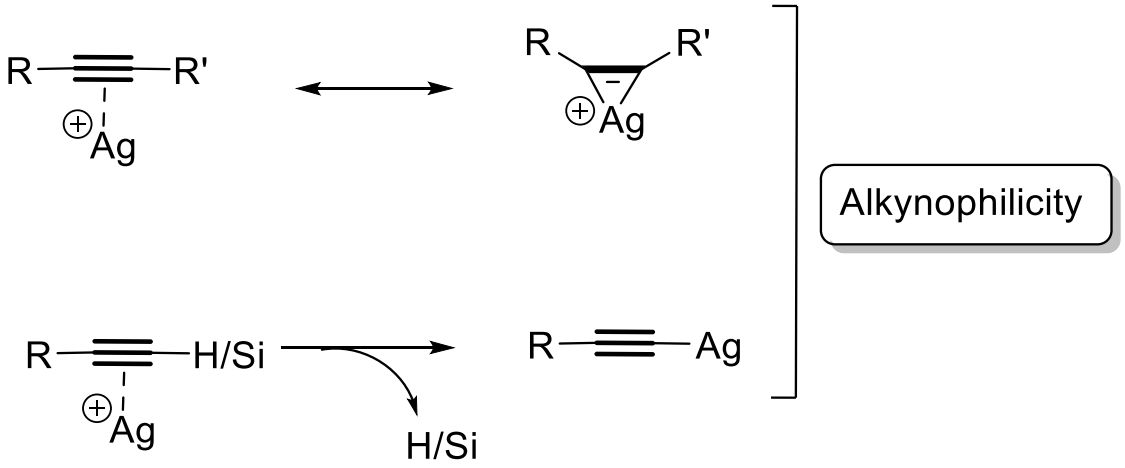


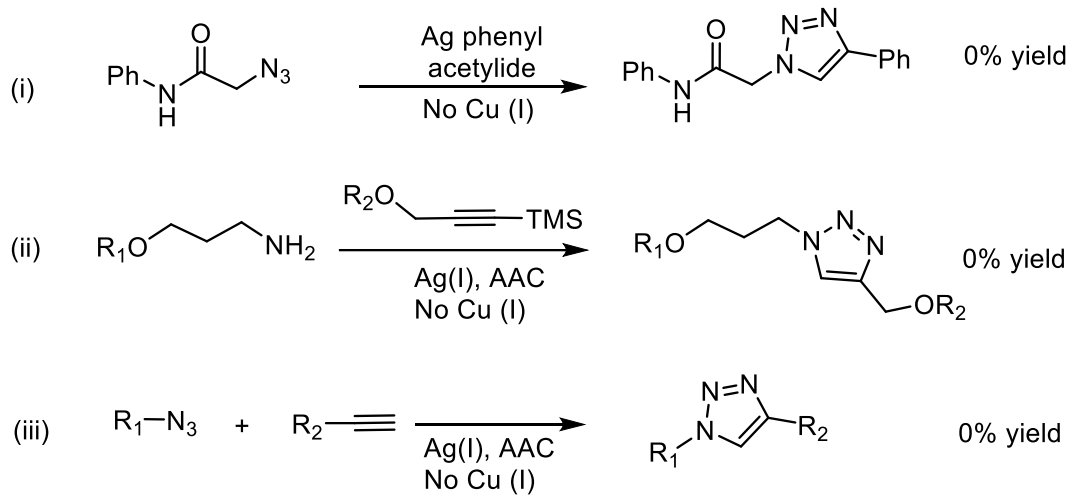
Figure 1.5: Activation of C-C triple bond by silver catalyst

1.5 Silver catalyzed azide-alkyne cycloaddition reaction (AgAAC):

As discussed earlier in **section 1.3** AAC reactions proceed through formation of copper acetylide. Study on gold (I), [18] silver (I) [19, 20] acetylides suggested that they participate in the AAC reaction.

However, the addition of copper (I) salts is required to effect the π-complexation step and subsequent cycloaddition. Several failed attempts have been reported for silver acetylides towards AAC reaction (Scheme 1.2).

For instance silver phenylacetylide when allowed to react with azides failed to promote cyclization in absence of copper [19].

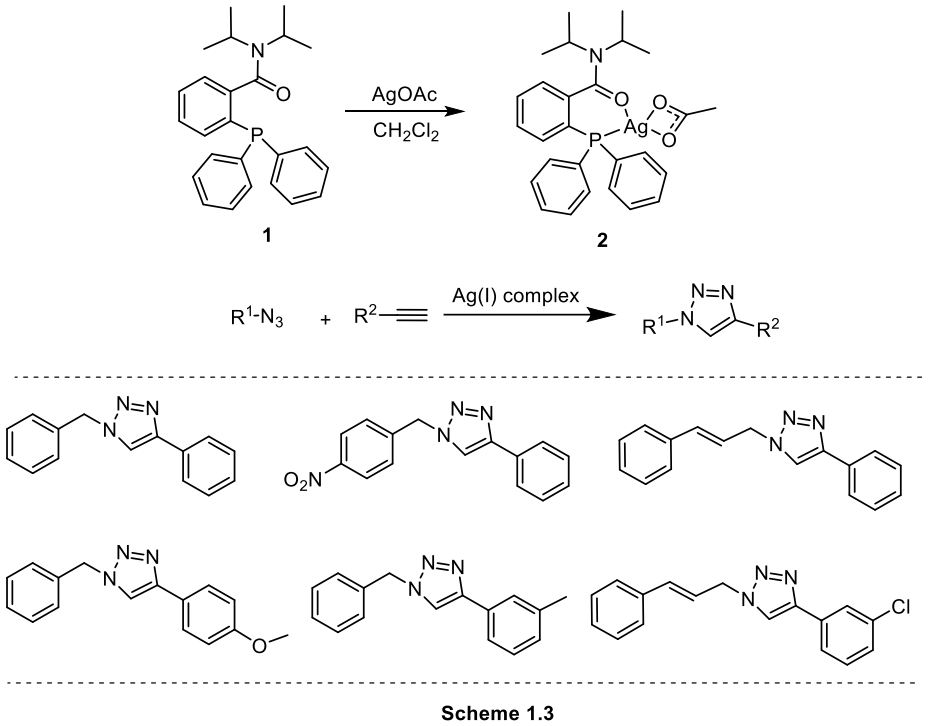


Scheme 1.2

Likewise, desilylation of a trimethylsilyl (TMS) alkyne with silver (I) generating the Ag-acetylide intermediate failed to react with azide [21]. However, in 2011 a successful attempt to purely silver catalyzed AAC has been made. After that many subsequent reports were made to study Ag catalysis towards click reaction or silver catalyzed azide-alkyne cycloaddition reaction which for our convenient will be addressed as AgAAC on the proceeding sections.

1.5.1 Ag (I) Complexes and Salts Used in AgAAC:

McNulty et al. have reported the first ever AgAAC reaction using P, O-type silver (I) complexes [22]. The complex 2 was synthesized from reaction of silver (I) acetate with 2-diphenylphosphino-N, N,-diisopropylcarboxamide ligand 1 and applied successfully for AgAAC of various azides and alkynes (**Scheme 1.3**).



Scheme 1.3

The mechanistic investigation of the reaction suggested existence of a silver acetylide but unlike CuAAC opposes alkyne π-complexation pathway in the initial step.

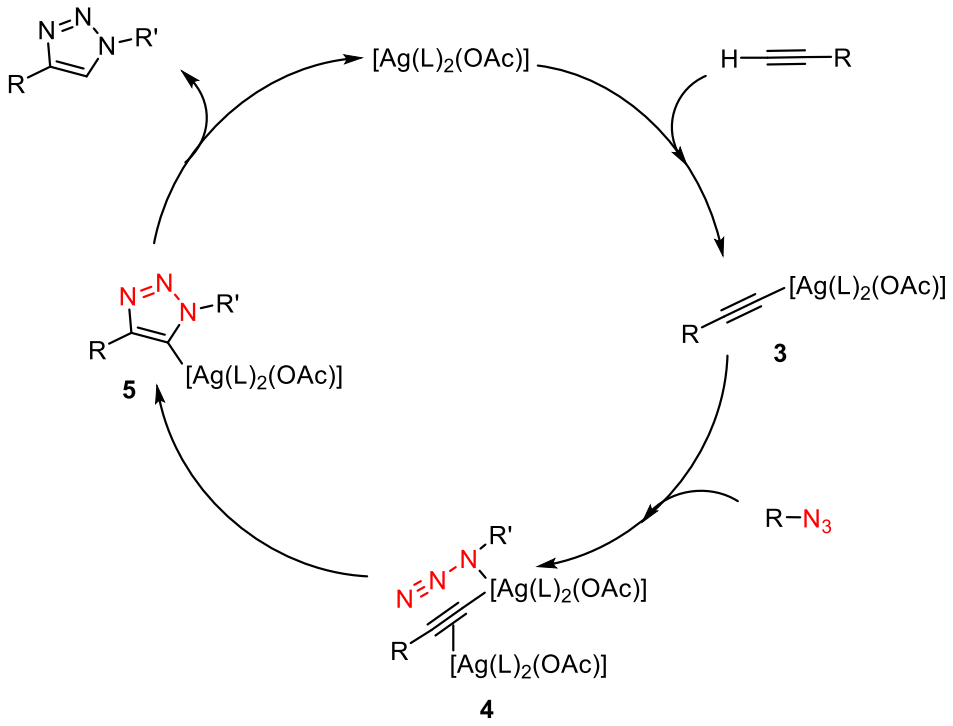


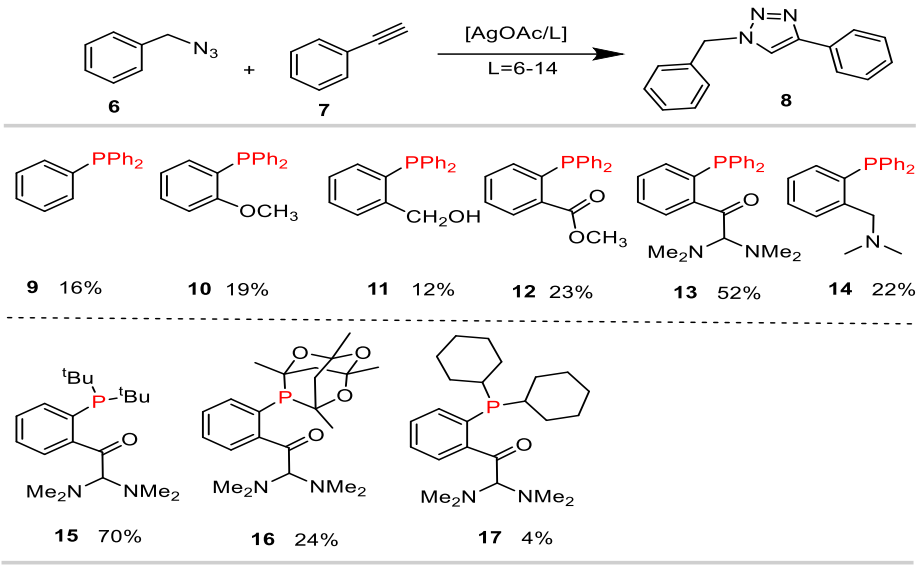
Figure 1.6: Mechanism of AgAAC catalyzed by silver (I) complex of P, O-type

At first the Ag complex forms an Ag-acetylide 3 with the alkyne and subsequently reacts with azide to generate a bimetallic π-complex species of type 4, wherein both metals are silver. This bimetallic π-complex thereafter forms a metalated triazole 5 which is then protonated to yield 1, 2, 3-triazole and regenerates the catalyst (**Figure 1.6**). The catalytic Ag (I) complex not only effects acetylide formation, but it also plays a pivotal role in further activation of the intermediate in order to effect cyclization.

In the previous study, reasonably high amount of silver catalyst (20 mol %) and significantly higher ratio (4.8:1) of azide substrate was used relative to alkyne to afford triazole products. To overcome these drawback the same group again came forward with a series of homogeneous Ag (I) ligand complexes to affect efficient click reaction [23]. By modifying ortho substituent in one phenyl ring of triphenylphosphine six first generation ligands **9-14** were synthesized (Scheme 4) and subsequently their Ag(I) complexes were crystallized with ligand and silver (I) acetate in 1:1 ratio. These Ag complexes show distinct effect of ortho substituents in the ligands in both catalysis and stability of the complexes.

The silver complex of **13** being the most stable shows good catalytic activity as shown in Scheme 1.4 and only minor depletion of Ag after completion of first cycle of reaction while Ag complex **11**, least stable among all Ag complexes stand out to be inefficient catalyst.

The amide substituted second generation ligands **15-17** when crystallized with Ag acetate renders better reactivity and stability. Out of all these complexes, one with tert-butyl substituted amide containing ligand **13** shows superior catalytic activity. These studies infer strong influence of ligands and stability of their corresponding complexes with silver towards AgAAC.



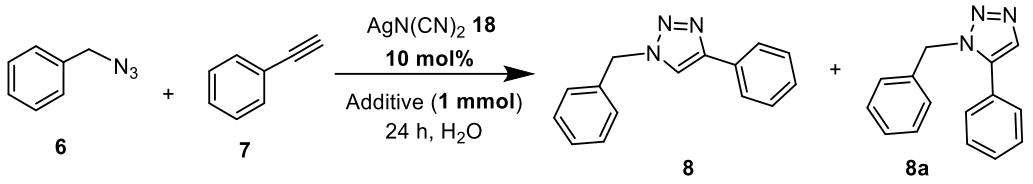
Scheme 1.4

Similarly, another simply prepared homogeneous Ag (I) complex, silver dicyanamide [AgN (CN) $_2$] **18** is found to be an active catalyst for AgAAC. Silver (I) dicyanamide complex is prepared by mixing equimolar mixture of $AgNO_3$ and NaN (CN) $_2$.

This Ag complex effectively generate triazole product. However, close inspection revealed formation of 1, 5-disubstituted-1, 2, 3-triazole alongside 1, 4-regioisomer. Further, incorporation of various additives seem to lower formation of 1, 5 regioisomer.

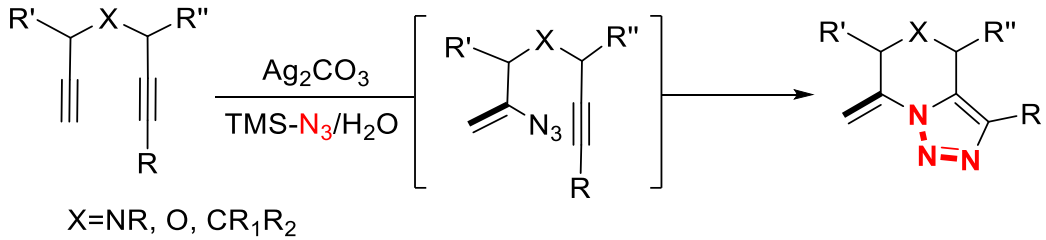
The effective additive was found to be diisopropyl ethylamine (DIPEA) as shown in Table 1.1. Further experiments showed 10 mol% of $AgN(CN)_2$, 1 mmol of DIPEA in combination with water/ethylene glycol solvent system effectively produced wide variety of 1,2,3-triazoles [24].

Table 1.1: Suppression of 1, 5 regioisomer formation by incorporation of additives



Catalyst (mol %)	Additive	Time	Isolated Yield (%)	
			8	**8a**
$AgN(CN)_2$	-	24h	40	10
$AgN(CN)_2$	L-proline	24h	54	0
$AgN(CN)_2$	$NHEt_2$	24h	55	0
$AgN(CN)_2$	NEt_3	24h	51	0
$AgN(CN)_2$	DABCO	24h	52	0
$AgN(CN)_2$	DBU	24h	56	0
$AgN(CN)_2$	**DIPEA**	**24h**	**70**	**0**
$AgN(CN)_2$	$(DHQD)_2PHAL$	24h	45	10
$AgN(CN)_2$	Pyridine-2-aldehyde	24h	43	13

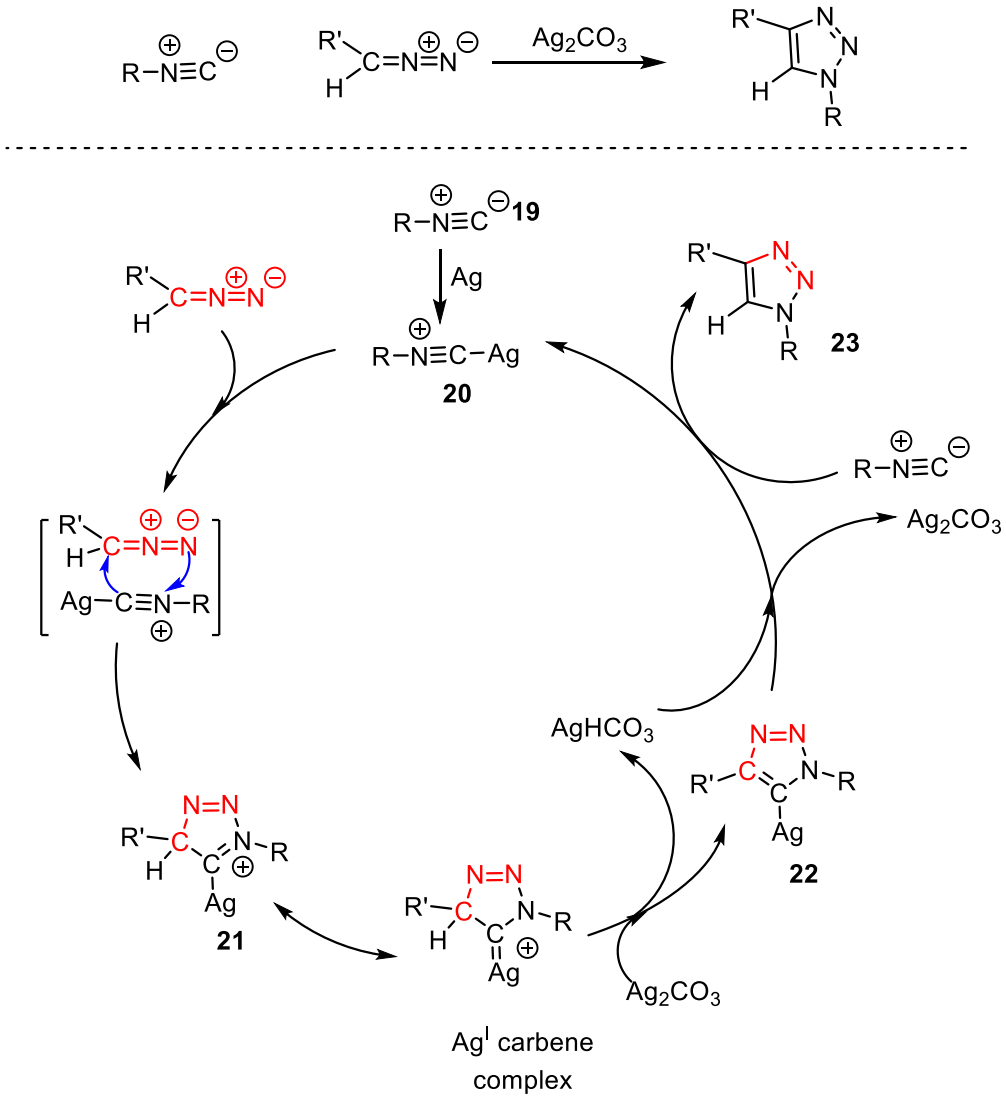
1.5-fused-1, 2, 3-triazole formation can be achieved by hydroazidation and subsequent alkyne-azide cycloaddition of diynes using silver carbonate as catalyst (Scheme 1.5) [25]. A wide variety of diynes participated in the reaction with trimethylsilyl azide (TMS-N_3) in the presence of H_2O, affording the corresponding 1, 5-fused- 1, 2, 3-triazoles in good-to-excellent yields.



Scheme 1.5

This method offers convenient synthesis of diverse pharmaceutically relevant 1, 5-fused 1, 2, and 3- triazole frameworks, including the fused heterocyclic units of piperidine, piperazine, morpholine, diazepine, and isoquinoline.

Isocyanides and diazo compounds also undergo 1, 3-dipolar cycloaddition under the influence Ag (I) catalyst to produce 1.4-disubstituted-1, 2, 3-triazoles (Scheme 1.6) [26].



Scheme 1.6

A plausible mechanism involves formation of silver isocyanide complex 20 by the reaction of the isocyanide **19** with silver (I). The cycloaddition between

complex **19** and diazo compound would give the intermediate **21** or Ag (I)-carbene complex. Subsequently, deprotonation of **21** with Ag_2CO_3 generates corresponding intermediate **22**. Further, protonation of **22** with $AgHCO_3$ finally produces the 1, 4-disubstituted 1, 2, 3-triazole **23** regenerating the silver complex **19**.

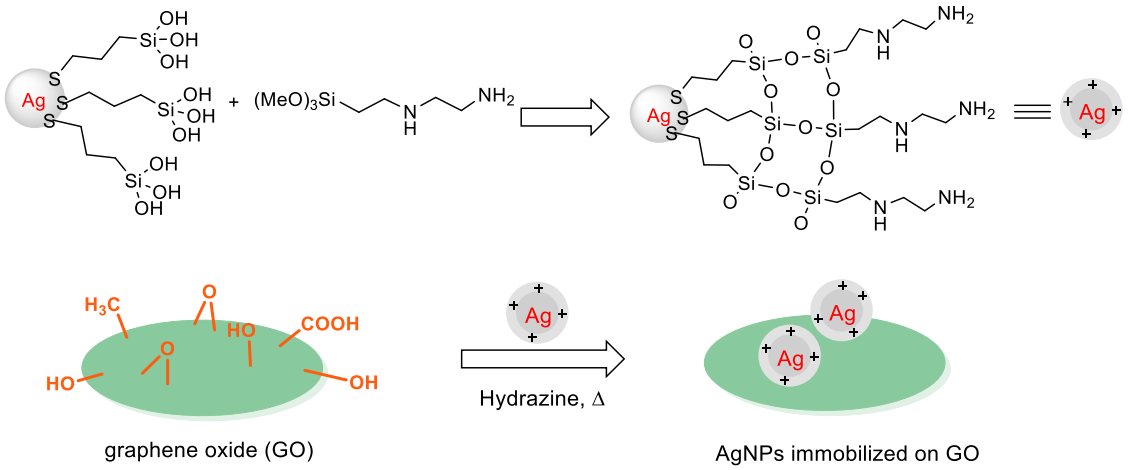
An interesting example of Ag catalyzed click reaction was demonstrated in cetylpyridinium chloride (CPyCl) mediated micellar media [27]. With catalytic amount of Ag_2CO_3 the AgAAC enjoys rapid reaction kinetics under influence of micellar solution.

After conducting preliminary investigation of the reaction, excellent product formation was observed with 10 mol% of Ag salt using water or ethylene glycol as reaction media. Typical organic solvents have not impacted much in turning the azides and alkyne into desired cycloadduct. However, incorporation of surfactant does the trick and shortens reaction time to 2 hour. Although effect of other surfactants is studied cetylpyridinium chloride remains superior in terms of triazole formation.

The optical microscopic image taken before and after charging the reacting material to the surfactant solution revealed micelle formation with spherical shape within which the hydrophobic reactants accumulate to finally transform into triazole products.

1.5.2 Ag Nanopartcles (Ag Nps) in AgAAC:

Metal nanoparticles (NPs) are popular catalysts in a number of organic transformations [28]. CuAAC has been successfully carried out with various Cu, Cu_2O and CuO NPs [29]. Graphene supported Ag NPs were applied successfully for AgAAC which is considered as first report of Ag NPs toward click reaction [30].



Scheme 1.7: Schematic representation of preparation of GO-AG nano composite

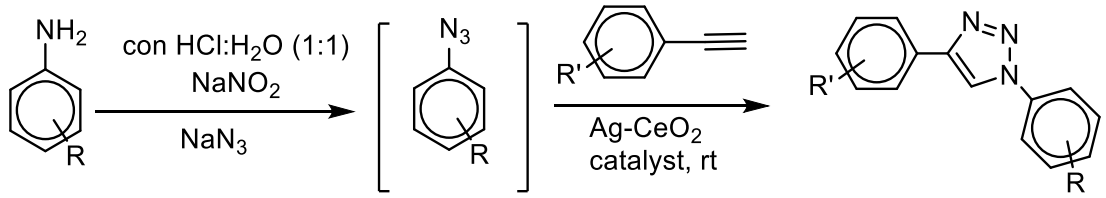
The catalyst is prepared by adding AgNPs to a stirred solution of graphene oxide (GO) and subsequent heating to 80^0C to cause precipitation (**Scheme 1.7**). The precipitate is filtered and washed with water to obtain GO Ag NPs nano composite and directly used in AgAAC of various azides and alkynes to obtain diverse 1, 4-disubstituted triazoles.

Ag_2O NPs is also used as catalyst for AgAAC reaction. However, use of Ag_2O NPs in case of azides particularly with electron-withdrawing substituents caused a loss of regioselectivity giving mixtures of 1, 4- and 1,5-substituted 1,2,3-triazoles [31]. This behavior depicts non click nature of this reaction. Similarly, polyallylamine resin based AgNP composite has been tested for alkyne-azide cycloaddition reaction by Zhao et al. [32].

This silver nanocomposite shows excellent catalytic activity at 80 °C for the synthesis of 1, 2, 3-triazoles. Islam and coworkers have reported synthesis of metallic Ag NP catalyst supported over Al_2O_3@Fe_2O_3 core-shell nanostructured material [33]. Initially colloidal Ag NPs are prepared by chemical reduction of alcoholic solution of $AgNO_3$ in tris (hydroxymethyl) aminomethane (THAM) with $NaBH_4$. Further nano colloidal AgNP solution is placed in a dispersion of Al_2O_3@Fe_2O_3 and sonicated to obtain Ag NP immobilized on Al_2O_3@Fe_2O_3.

This nano catalyst is successfully applied for synthesis of various triazoles. Furthermore, Bala and Islam et al. reported room temperature synthesis of AgNP supported on modified CeO2 3D porous nano cubes [34].

The surface of ceria nanocubes were modified with 2, 4-dimethyl phenol (DMP). Ag-CeO_2 was efficiently applied for one pot synthesis of 1,2,3-triaoles from aromatic amines through in situ azide formation by diazotization reaction and triazoles formation by subsequent addition of terminal alkyne (Scheme 1.8).



Scheme 1.8

1.5.3 Multi Component Reaction for AgAAC:

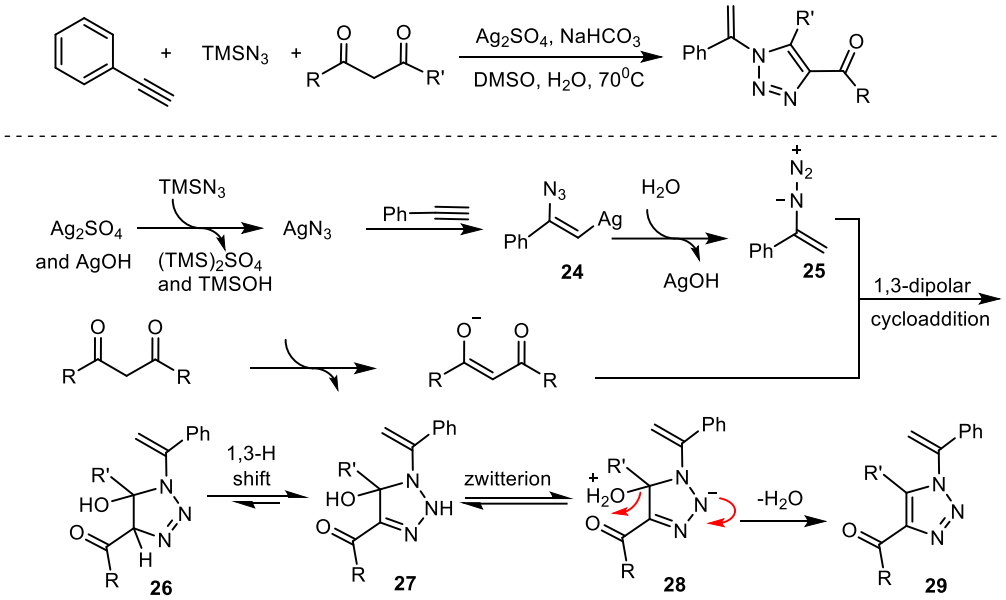
One of the major challenges in organic synthesis is the creation of diverse complex molecular architecture from simple and readily available substrates.

Therefore, processes that allow formation of several bonds within single operational step are highly welcomed. Multicomponent reactions (MCR), involve condensation of more than two reactants to form a product that feature significant portions of all reactants.

Zhang et al. have reported a silver-mediated three component cycloaddition reaction of phenyacetylenes, trimethylsilylazide, and 1,3-dicarbonyl compounds which enables the preparation of various substituted 1-N-vinyl-1,2,3-triazoles [35].

The mechanistic investigation suggested initial formation of AgN_3 with liberation of TMS_2SO_4 and TMSOH (**Scheme 1.9**).

TMS_2SO_4 is generated by anion exchange between $TMSN_3$ and Ag_2SO_4 while in basic medium TMSOH is produced instead of TMS_2SO_4. Further vinyl azide 25 is formed by insertion of AgN_3 to the alkyne and subsequent protodemetelation of silver vinyl intermediate 24 with water.

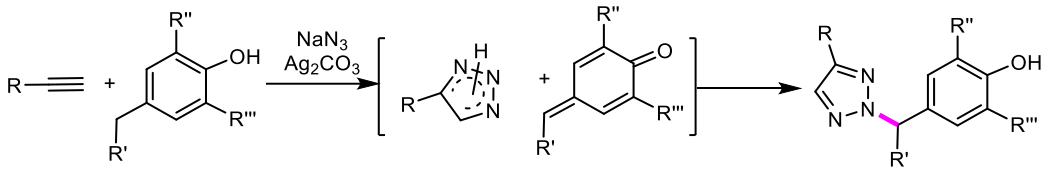


Scheme 1.9

This intermediate **25** undergoes 1, 3-dipolar cycloaddition with the enolate obtained from the diketone with the action of base to produce vinyl triazoles intermediate **26**. Intermediate **26** undergoes zwitter ion formation followed by dehydration to yield final vinyl triazole 29.

N^2-sunstituted-1, 2, 3-triazoles preparation can be achieved by multicomponent Ag (I) catalyzed reaction of terminal alkyne, sodium azide and trisubstituted phenol [36].

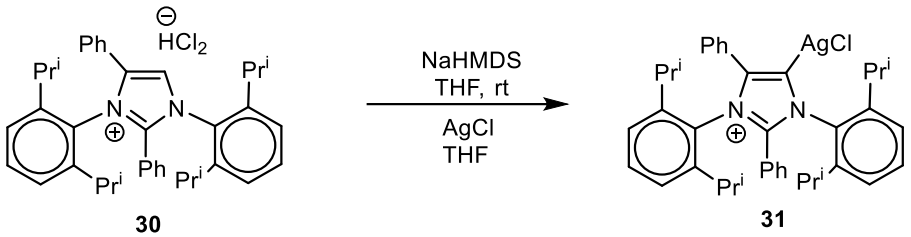
The reaction proceed via in situ generation of NH-1, 2, 3-triazole which consequently undergoes direct benzylic amination to produce N^2-sunstituted-1, 2, 3-triazole (Scheme 1.10). In this process both source of amination and electrophiles are generated in situ.



Scheme 1.10 **N^2-substituted triazoles**

1.5.4 N-Heterocyclic Carbene Complex in AgAAC:

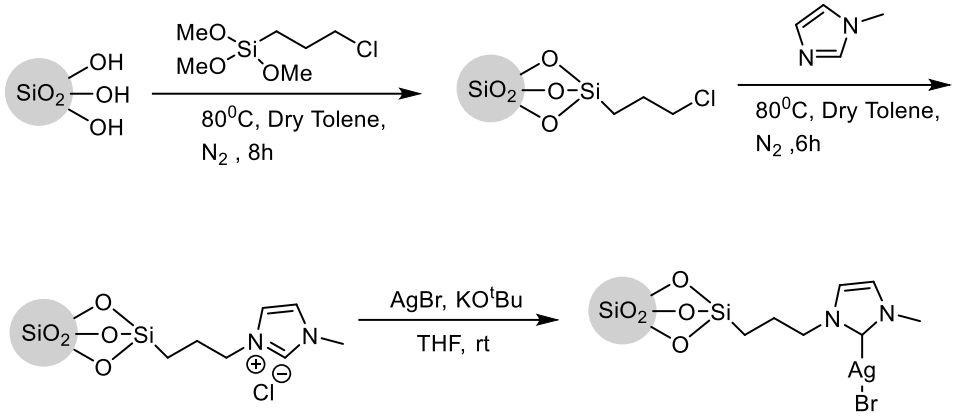
N-heterocyclic carbenes with their strong σ-donation and weak □-acceptor ability make them an attractive class of ligand for various transition metal based complexes [37]. Ag-NHC compounds have long been used as NHC transfer agents for their stability towards moisture, air and ease in synthesis [38]. Ortega-Arizmendi et al. [39] reported the first case of Ag-NHC complex as catalyst for click reaction. The Ag-NHC complex 31 was prepared by treatment of 1, 3-bis-(2, 6-diisopropylphenyl)-2,4-diphenylimidazolium chloride 30 with sodium bis(trimethylsilyl)amide (NaHMDS) and AgCl at room temperature (Scheme 1.11). This Ag-NHC catalyst in very small amount (0.5 mol %) can efficiently produce 1, 2, 3-triazoles while under similar condition 5 mol% AgCl is required to produce similar effect.



Scheme 1.11

Our group synthesized a silica immobilized Ag-NHC catalyst by anchoring coordination technique [40]. For preparation of the catalyst pre activated silica is first functionalized with 3-chloropropyltrimethoxysilane (CPTMS) wherein 1-methylimidazole is attached in the next step. These steps are performed in dry toluene under inert atmosphere. Further treatment of the functionalized silica with AgBr in presence of potassium tert-but oxide in THF finally result desired silica

immobilized Ag-NHC catalyst (Scheme 1.12). This catalyst shows excellent catalytic performance towards AgAAC to form variety of 1, 4-disubstituted-1,2,3-triazoles with metal loading as slow as 0.006 mol%.



Scheme 1.12

Catalytic superiority of these Ag-NHC are attributed to the property of NHC ligand to stabilize Ag(I) ion as well as Ag-acetylide formed during the course of the reaction.

1.5.5 AgAAC and Computational Study:

After several successful endeavors with Ag (I) species catalyzed click reaction, mechanism of AgAAC reaction has been studied by quantum mechanical calculations. Proper investigation of the reaction mechanism will offer more control over the synthesis and help to obtain complex molecular architecture without involvement of copper species. The validity of the experimentally suggested reaction mechanism was studied by modelling the intermediates and the transition state structures connecting them. The Density Functional Theory (DFT) calculations with both B3LYP with 6-31G basis set [41] and ωB97XD functional with MWB28 effective core potential and 6-31+G* basis set [42] show that once the silver acetylide structure forms, spontaneous triazoles formation take place. The major concern regarding the mechanism is the no of Ag atom that take part in the mechanistic steps. Hence, both mono- and binuclear pathways for

the reaction have been taken into account in these studies. It was concluded that the energy barrier for the binuclear pathway is lower than that mononuclear case.

1.6 Conclusion:

In this chapter click reaction is discussed in view of Ag catalysis. Various Ag catalyzed synthetic strategies for triazoles synthesis and their plausible mechanisms are discussed. Although copper could be more convenient for 1, 2, 3-triazole synthesis however its cytotoxic nature limits its suitability in terms of bio medicinal application. Silver being non-toxic can be the best alternative to copper catalyzed bio orthogonal click reaction. Hence AgAAC that gives a direct access to 1, 4-regioisomers of 1, 2, 3-triazoles eliminating the need of redox active copper (I) species opens a new era of exciting perspectives in organic synthesis, material science and pharmaceutical industry.

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