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Gold-Catalyzed Cycloisomerization of Ortho-Nitro-Alkynylbenzene: Mechanistic Developments

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Abstract

Gold catalysis has emerged as a pivotal area in modern organic synthesis, offering novel reactivity patterns and enabling the construction of intricate molecular architectures that were once considered challenging or inaccessible. While traditionally regarded as inert, the unique electronic properties of gold, particularly its propensity for π-acid activation and tolerance towards a wide range of functional groups, have propelled it to the forefront of modern catalysis. In recent decades, the exploration of gold catalysis has led to the development of a plethora of innovative synthetic methodologies, revolutionizing the way chemists' approach complex molecule synthesis. Historically, gold was perceived as a noble metal with limited reactivity in organic transformations. However, pioneering work by Toste, Hashmi, and others in the early 2000s demonstrated that gold complexes could catalyze a diverse array of organic reactions, including formation of carbon-carbon as well as carbon-heteroatom bonds, cycloisomerizations, and rearrangements. This paradigm shift challenged conventional wisdom and opened up new avenues for leveraging gold as a catalyst in organic synthesis. The exceptional reactivity exhibited by gold catalysts can be attributed to several key factors. Unlike transition metals such as palladium or platinum, which typically operate in high oxidation states, gold commonly operates in low oxidation states, facilitating π-acid activation of unsaturated substrates. Additionally, gold complexes exhibit a high degree of coordination flexibility, enabling them to adopt diverse coordination geometries and accommodate a wide range of substrates. Furthermore, gold complexes are often air- and moisture-stable, making them practical and user-friendly catalysts in synthetic laboratories.

Keywords: *Cycloisomerization; Gold-Catalysis; Hetero-Atom Transfer; 2-Nitro-Alkynylbenzene; Reaction Mechanism*

Introduction

Gold catalysis has gained significance in synthetic organic chemistry, offering a valuable technique to selectively modify carbon-carbon multiple bonds. One of the hallmark features of gold catalysis is its ability to activate alkynes, alkenes, and allenes, leading to the formation of C–C and C-hetero-atom bonds under mild reaction conditions

(Stylianakis & Kolocouris, 2023). The activation of unsaturated bonds by gold typically proceeds through a π- bond coordination followed by nucleophilic addition of carbon or heteroatom nucleophiles to form C-C and C-hetero-atom bonds (Kumar, Kaliya & Maurya, 2023). Co-ordination of gold with π-bond can stabilize the LUMO thus reducing the HOMO-LUMO energy barrier and facilitating the reaction. This unique reactivity has enabled the development of highly efficient and selective transformations that were previously inaccessible using traditional transition metal catalysts (Witzel, Hashmi & Xie, 2021). The broad scope of gold-catalyzed reactions encompasses a wide range of synthetic transformations, including cycloadditions (Zhang *et al*., 2020), cross-couplings (Panda & Sarkar, 2010, 2013; Nijamudheen & Datta, 2020), cycloisomerizations (Praveen, 2021; Tzouras *et al*., 2023), pericyclic reactions (He, Jana & Koenigs, 2020), cross-dehydrogenative coupling (oxidative coupling) (Panda, 2020; Zheng *et al*., 2021) and cascade reactions (Ghosh & Bhakta, 2023). These reactions have found applications in various areas of organic synthesis, including natural product synthesis (De *et al*., 2022), pharmaceutical chemistry (Soklou *et al*., 2022) and materials science (Hendrich *et al*., 2021). Furthermore, the ability of gold catalysts to operate under mild conditions and tolerate functional groups makes them valuable tools for late-stage functionalization and complex molecule synthesis.

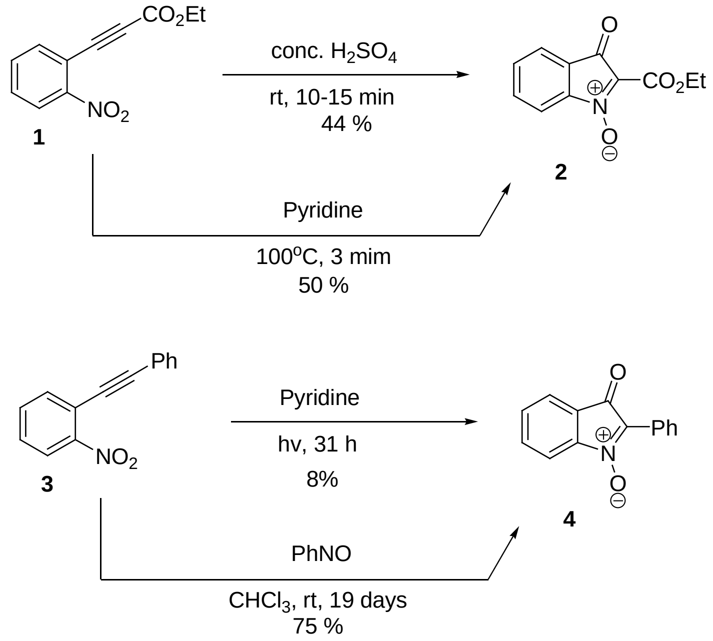
Cycloisomerization reactions represent a class of transformations that hold significant importance in the synthesis of complex organic molecules (Panda, 2019). By efficiently constructing cyclic structures from simple starting materials, these reactions offer atom-economic pathways towards the synthesis of diverse structural motifs. The ability to access a wide array of cyclic compounds through cycloisomerization reactions has found applications in various fields, including natural product synthesis, pharmaceutical chemistry, and materials science. As such, understanding the mechanisms underlying these transformations is crucial for developing efficient synthetic methodologies and unlocking new avenues for chemical synthesis. Heterocyclic compounds are highly important classes of compounds due to their inherent biological activities. Gold catalysis was found to be efficient for the synthesis of various heterocyclic compounds (Kadiyala *et al*., 2024).

On the other hand, ortho-nitro-alkynylbenzenes have emerged as versatile substrates in metal-catalyzed cycloisomerization reactions due to their structural diversity and synthetic utility. These substrates possess an ortho-nitro group and an alkynyl functionality attached to a benzene ring, providing multiple handles for diversification and subsequent elaboration into complex cyclic structures. The cycloisomerization of ortho-nitro-alkynylbenzenes has garnered considerable attention in recent years, owing to its potential for accessing biologically active compounds and heterocyclic scaffolds with high efficiency and selectivity.

The primary intend of this chapter is to give a comprehensive overview of the mechanistic developments in gold-catalyzed cycloisomerization reactions of ortho-nitro-alkynylbenzenes. By elucidating the intricate mechanistic pathways involved in these transformations, this chapter aims to deepen the understanding of the reactivity patterns of gold catalysts and shed light on the factors governing their catalytic activity and selectivity. It is anticipated that this chapter will contribute to the advancement of gold catalysis and stimulate new avenues for chemical synthesis and discovery.

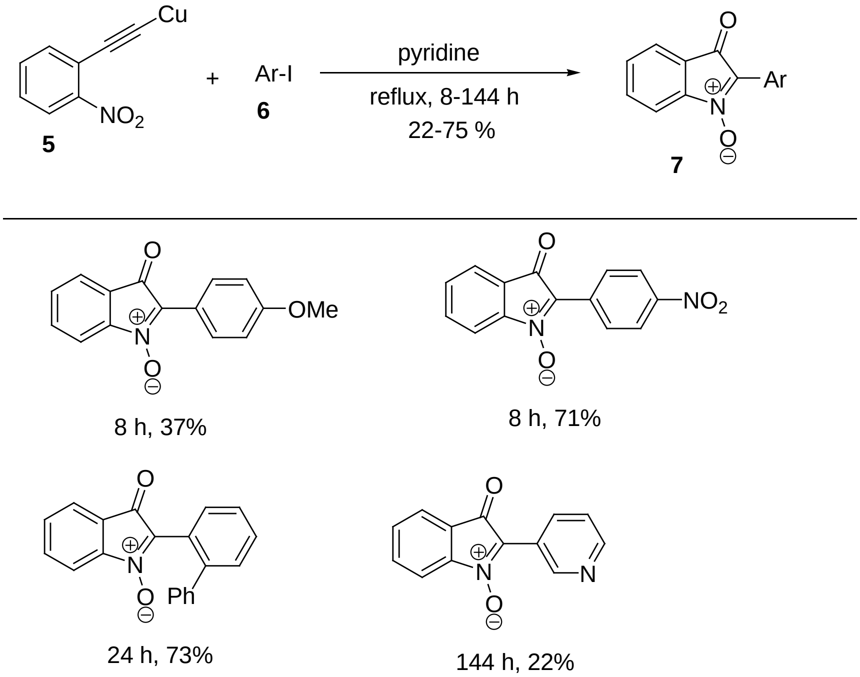
Results and Discussion

The cyclization reaction of o-alkynylnitrobenzenes represents one of the earliest documented redox processes in organic synthesis. In 1882, Baeyer reported the cycloisomerization of o-nitrophenylpropiolates 1 in cold concentrated sulfuric acid as part of the synthesis of indigo, resulting in the formation of 2-carboxy-3-oxo-3Hindole 1-oxide 2. This compound's central bicyclic core is commonly referred to as an isatogen (derived from "isatin" and "gen"), as it is isomeric to isatin. Subsequently, Pfeiffer (1916) and Ruggli, Caspar and Hegedüs (1937) systematically investigated this type of compound and made significant progress in o-nitroalkyne cycloisomerization. Their work included the utilization of pyridine-mediated internal redoxycyclization reactions under photochemical or thermal conditions (Scheme 1), as well as the application of nitrosobenzene as a promoter in the cycloisomerization process, which required several days for the formation of the isatogens.

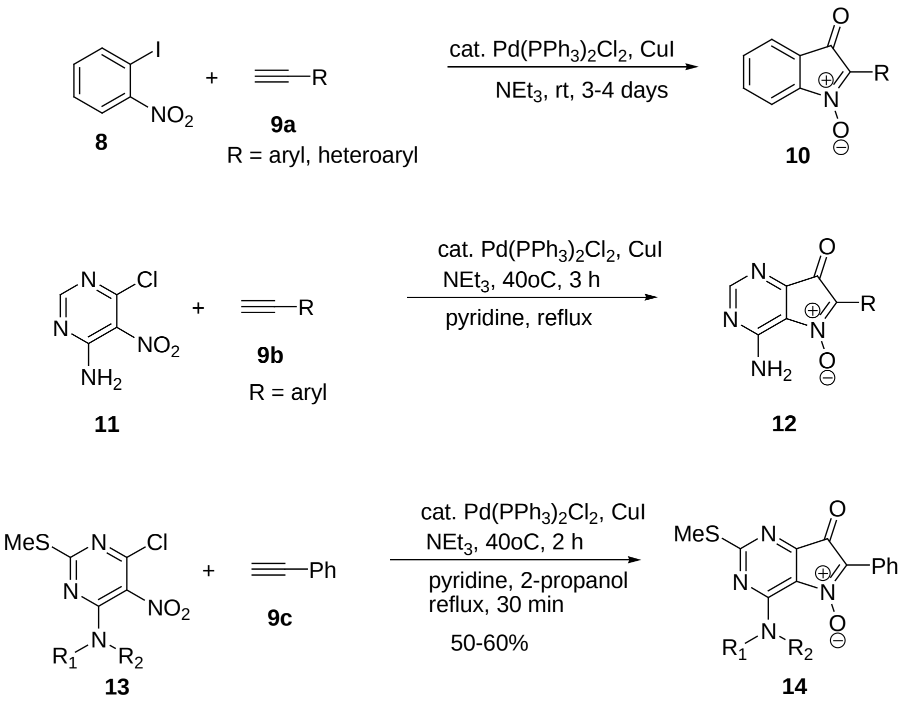


Scheme 1: Cycloisomerization of Nitroalkynes under various conditions

In 1969, Bond and Hooper made a significant observation while preparing unsymmetrical diaryl acetylenes using Cu(I) 2-nitrophenylacetylide 5 under Castro-Stephens coupling conditions. They found that in certain cases, heating of the reaction for long time in pyridine directly yielded the heterocyclic compound isatogens 7 (Scheme 2). In that case, the yields and reaction times varied depending on the substituents bearing on the aromatic ring. In a similar vein, Rosen and co-workers (2000) detailed a one-pot procedure involving the Sonogashira coupling of 2-iodonitrobenzene derivatives 8 with terminal alkyne 9a in neat triethylamine, followed by pursuing the reaction for 3–4 days at room temperature as shown in Scheme 3. This methodology has been effectively utilized for synthesizing various 2-hetero-aryl isatogens 10. It has been found that, when the terminal alkyne contains an alkyl group (e.g. methyl) on the alkyne terminus, the corresponding 2-methylisatogen was afforded in low yields. While the precise function of the actual Pd-catalyst in the cyclization remains somewhat ambiguous, the simplistic nitroalkyne cycloisomerization at room temperature suggests that the phosphine-free Pd(II)-salts formed after the initial Sonogashira coupling may play a significant role. Interestingly, a comparable protocol with 6-chloro-5-nitropyrimidine derivatives 11/13 necessitated separate heating in neat pyridine to facilitate the necessary nitroalkyne cycloisomerization (Susvilo, Brukstus & Tumkevicius, 2003; Cikotiene, Pudziuvelyte & Brukstus, 2008).

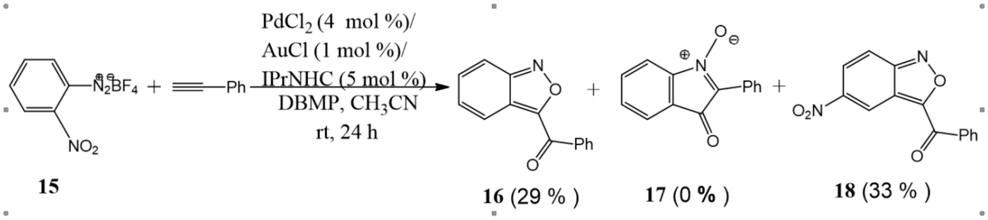


Scheme 2: Tandem Stephen-Castro coupling and cycloisomerization reaction



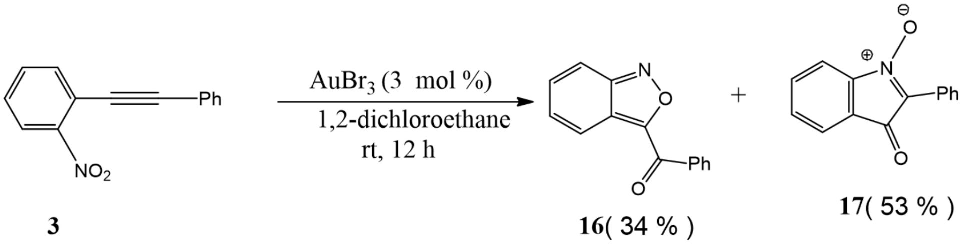
Scheme 3: One-pot tandem Sonogashira coupling –cycloisomerization reaction

In 2010, the team reported the first Sonogashira coupling of arenediazonium salts with terminal alkynes using a catalytic amount of both $PdCl_2$ and AuCl in the presence of an NHC ligand (Panda & Sarkar, 2010). This unique finding generates great attention to the chemical community and results in further development of more than ten protocols within ten years (Panda, 2021). During this work, the researchers found that when ortho-nitrobenzenediazonium salts were used in the Sonogashira coupling reaction, instead of forming the expected coupling product, the reaction underwent a tandem cyclization catalyzed by gold, leading to the formation of anthranils.



***Scheme 4**: Tandem Sonogashira coupling and cycloisomerization reaction*

The coupling of 2-nitrobenzenediazonium tetrafluroborate 15 with phenylacetylene gave the anthranil 16 in 29% yield, accompanied by nitro-anthranil 18 (33 %); however, no trace of the isatogen 17 could be detected in the crude reaction mixture (Scheme 4).



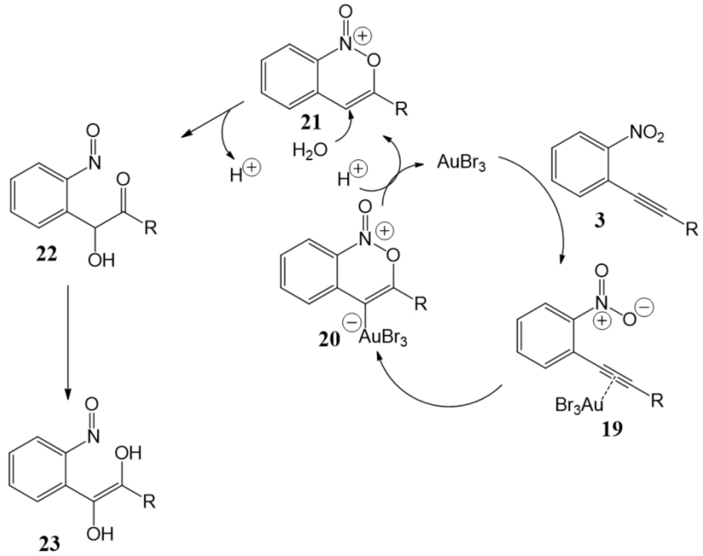
Scheme 5: Gold catalyzed cycloisomerization of 2-nitroalkyne

Table 1: *Summary of synthesis of isatogens*

Substrate(s)	Scheme	Reagent/ Catalyst(s), Temp.	Base/Additive	Ref.	Authors
Nitroalkynes	1	c. H_2SO_4, rt	Nil	19	Baeyer (1882)
Nitroalkynes	1	Pyridine, 100 °C	Nil	19	Baeyer (1882)
Nitroalkynes	1	Pyridine, hv	Nil	20	Pfeiffer (1916)
Nitroalkynes	1	PhNO, rt	Nil	21	Ruggli, Caspar and Hegedüs (1937)
Cu(I) 2-nitro-phenylacetylide and aryl iodides	2	Pyridine, reflux	Nil	22	Bond and Hooper (1969)
1-Iodo-2-nitrobenzene and aryl acetylenes	3	cat. $Pd(PPh_3)_2Cl_2$, CuI, rt	Et_3N	23	Rosen *et al*. (2000)
6-chloro-5-nitropyrimidine derivatives and aryl acetylenes	3	cat. $Pd(PPh_3)_2Cl_2$, CuI, 40 °C	Et_3N, Pyridine	24	Susvilo, Brukstus and Tumkevicius, (2003)
6-chloro-5-nitropyrimidine derivatives and phenylacetylene	3	cat. $Pd(PPh_3)_2Cl_2$, CuI, 40 °C	Et_3N, Pyridine, 2-propanol	25	Cikotiene, Pudziuvelyte and Brukstus
Nitroalkynes	5	cat. $AuBr_3$, rt	Nil	28	Asao, Sato and Yamamoto (2003)

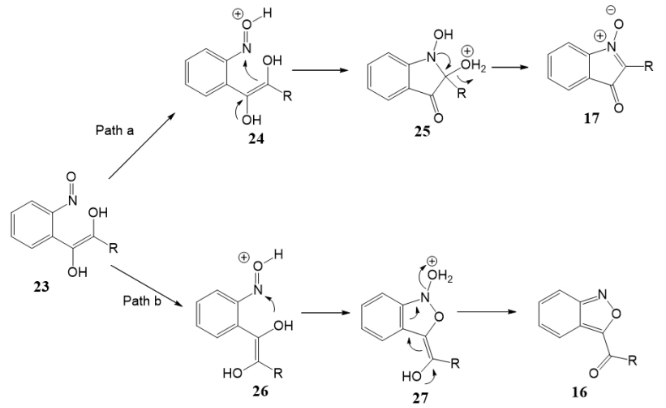
The gold-catalyzed cycloisomerization of nitrotolans, as detailed by Asao and co-workers in 2003 (Scheme 5), marks a significant stride in the synthesis of 2-arylisatogens. It's noteworthy that when the pendant alkyne substituent is an alkyl group, an internal redox process takes place in a complementary manner, leading to the formation of benzo[c]isoxazole, commonly known as anthranil. On the other hand, when the pendant alkyne substituent is an aryl group, this cycloisomerization reaction yielded isatogen as major product. Table 1 summarizes the various methods used for the synthesis of isatogens through the cycloisomerization of 2-nitroalkynes.

Asao, Sato and Yamamoto (2003) suggested a mechanism for the gold catalyzed cycloisomerization of 2-nitroalkynes through the addition of the oxygen atom from the nitro group in a 6-endo-dig fashion as the pivotal step in the intramolecular redox process (Scheme 6). The coordination of the triple bond of compound 18 to $AuBr_3$ boosts the electrophilicity of the alkyne. This sets the stage for a nucleophilic attack by the oxygen atom of the nitro group onto the electron-deficient alkyne, resulting in the formation of an intermediate auric ate complex 20. Initially, it was proposed that the resulting gold-ate complex 20 undergoes protonolysis, followed by ring opening with water, leading to the formation of nitrosobenzene 23. In the reaction medium, even a trace amount of water can generate a proton due to the presence of $AuBr_3$. Subsequently, two potential pathways for the subsequent dehydrative cyclization have been suggested, leading either to isatogens (path a) or anthranil (path b). While this elucidates the potential pathways, it fails to explain why these pathways are dependent on the substituents present.



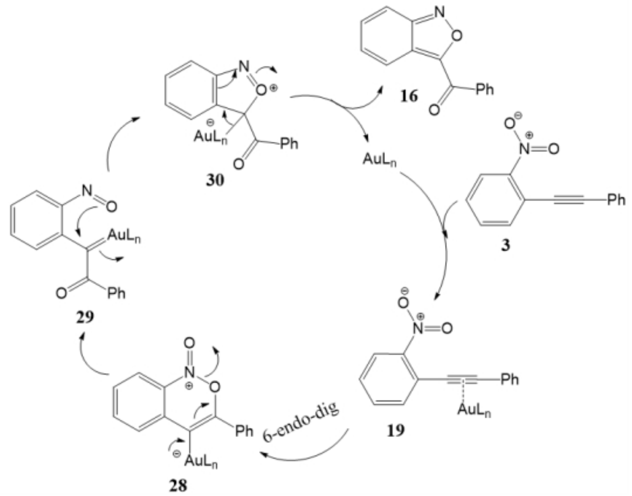
Scheme 6: *Yamamoto's postulated mechanism of gold catalyzed cycloisomerization of 2-nitroalkynes*

The formation of isatogen 17 involves a cyclization process of compound 24, followed by the elimination of water, as depicted in Scheme 7 (path a). Conversely, if the reaction progresses along path b, anthranil 16 is generated through the intramolecular nucleophilic addition of the enol oxygen, succeeded by water elimination.

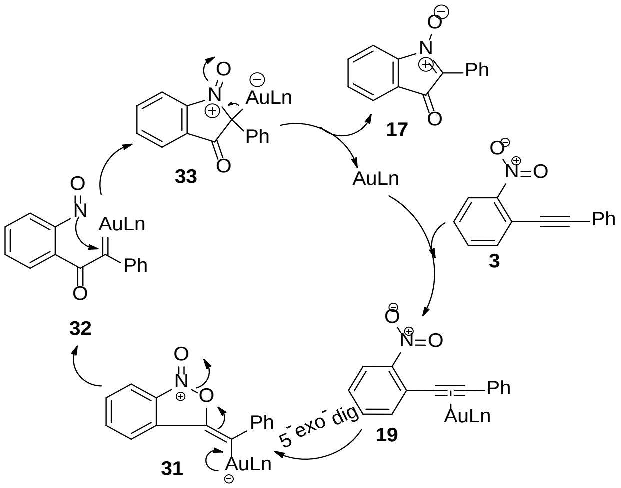


Scheme 7: Yamamoto's postulated mechanism for the formation of isatogens and anthranils

However, their proposal is notably different from those given by Asao, Sato, and Yamamoto (2003), as the reaction was carried out under strictly anhydrous conditions to furnish the desired products. A plausible mechanism for the formation of the anthranils 16 and isatogen 17 from 3 is given in Scheme 8 and 9; thus, the gold (I) coordinated triple bond of the Sonogashira product 3, that is 19, encourages nucleophilic attack by the neighbouring nitro group, thereby forming the auric ate complex 28; ring opening to gold carbenoid 29 followed by its capture by the nitroso group and elimination of the catalyst from 30 gives the anthranil 16. Similarly, addition of nitro-group to the coordinated alkyne intramolecularly via 5-exo-dig fashion provides complex 31, which then rearranged to gold carbene 32. Now addition of nitroso group to the gold carbene and subsequent rearrangement resulted in isatogen 17. This work was presented at the NOST conference on May 4, 2009, in Goa, India.



Scheme 8: Panda's postulated mechanism of gold catalyzed synthesis of anthranil



Scheme 9: Panda’s postulated mechanism of gold catalyzed synthesis of isatogen

Later, density functional theory (DFT) calculations were conducted by Vipin Raj and co-workers (2021) to investigate the internal oxygen transfer in Au-catalyzed o-nitroalkyne cycloisomerization reactions, aiming to elucidate the relative energies associated with this process as well as the resulting α-oxo gold carbenes. These calculations provided clear insights into the thermodynamic stability of the α-oxo gold carbenes generated from the 6-endo dig addition of oxygen to the alkyne, in comparison to the alternative α-oxo gold carbene formed from the 5-exo dig addition. Additionally, their computational analysis suggests that substitutions on the o-nitroalkynes play a significant role in modulating the regio-selectivity of the reaction, thereby influencing the outcome of the cycloisomerization process. This study supports the researchers' speculation regarding the mechanism of gold-catalyzed cycloisomerization of o-nitroalkynes. Moreover, Dhote and Ramana (2021) successfully trapped the α-oxo gold carbenes intermediate using electron-rich anthranils, leading to the formation of highly functionalized 3-acyl-(2-formylphenyl)-2H-indazoles via sequential carbon-oxygen, carbon-nitrogen, and nitrogen-nitrogen bond formations. This observation provides indirect evidence supporting the existence of α-oxo gold carbenes in the [Au]-catalyzed internal redox processes of nitroalkynes (Dhote, Halnor & Ramana, 2021).

The preceding discussion highlights Yamamoto’s report on Au-catalyzed nitroalkyne cycloisomerization, which has reignited interest in this field. This process leads to the synthesis of isatogens, offering a pathway for the facile functionalization of these compounds at the C2-position. This functionalization can occur through either nucleophilic addition or cycloaddition, yielding the synthetically valuable 2,2-disubstituted 1,2-dihydro-3H-indolin-3-one skeleton, commonly referred to as pseudoindoxyl—a subgroup within the indole group of alkaloids (Liu *et al.*, 2015). Researchers have been particularly inspired by the versatility of this skeleton, as evidenced by the emergence of a variety of Pd, Cu, Ag, and Hg complexes aimed at developing regioselective nitroalkyne cycloisomerizations (Xie *et al*., 2021). However, the use of [Au]-complexes in these cyclizations holds particular appeal due to their facile operation at room temperature. Additionally, [Au]-complexes offer the advantage of Lewis acidity, which not only enables post-functionalization of the resulting isatogens but also opens avenues for employing other Lewis acids in tandem reactions, leading to the development of novel cascade and one-pot processes.

Conclusion

Understanding the reaction mechanism of a catalytic organic reaction is particularly crucial due to the pivotal role that catalysts play in these processes. Catalytic reactions occur with the assistance of a catalyst, which accelerates the reaction rate without being consumed in the process. By understanding the mechanism, chemists can optimize catalyst design and reaction conditions to enhance reaction efficiency and selectivity. Additionally, knowledge of the mechanism allows for the development of more sustainable and environmentally friendly catalytic processes by minimizing waste and energy consumption. Furthermore, understanding the intricacies of catalytic reactions facilitates the discovery of new catalytic systems and the improvement of existing ones, driving advancements in synthetic chemistry and catalysis research. In this chapter, we have shown that gold catalysed cycloisomerization reaction is feasible strictly in the absence of water, which is in contrary to Yamamoto’s findings. The researchers have thoroughly discussed their previously proposed cycloisomerization reaction mechanism, which involves a gold carbenoid intermediate for the synthesis of anthranils and isatogens from 2-nitroaryl alkynes in the presence of a gold catalyst.

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