Catalytic reactions involving the cleavage of carbon–cyano and carbon–carbon triple bonds

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The catalytic reactions that involve the cleavage of C–CN bonds and carbon–carbon triple bonds are described in this *tutorial review*. Regarding the cleavage of a C–CN bond, the catalytic reaction can proceed by two different mechanisms: oxidative addition and deinsertion of silyl isocyanide. A carbon–carbon triple bond can be cleaved in the absence of an organic promoter *via* the formation of unique organometallic species, such as allenylidene and cyclopropyl carbenoid complexes.

1. Introduction

Among the chemical bonds that are unreactive to chemical transformation, carbon–carbon (C–C) bonds, because of their thermodynamic stability, remain the most challenging. Thus, the activation of C–C bonds generates a lot of interest in the field of organometallic chemistry. To make this unfavorable process thermodynamically feasible, two approaches should be considered: 1) increasing the energy state of the starting material, and 2) lowering the energy state of the C–C bond cleavage product.[1,2] The first approach can be enhanced by employing strained molecules, such as cyclopropanes and cyclobutanes, the reactions of which are driven by the relief of the ring strain. The second approach represents the utilization of chelation-assistance, in which the appropriately located coordinating group attracts the metal complex in proximity to the C–C bond to be cleaved and the stable metallacycle (typically five-membered) is formed. Although these two approaches are the most powerful in stoichiometric systems, difficulties may be encountered when they are applied to the catalytic reactions. To establish a catalytic reaction, the stable organometallic species, typically formed *via* the metal insertion into small rings or cyclometallation, must further react. The final organic product must be produced from the formation of the chemical bonds that are more stable than the cleaved C–C bond. The difficulty in producing the C–C bond is evident, so systems must be designed so that the C–C bonds in the product are more stable than those in the starting material. This is in sharp contrast to the catalytic C–C bond formation through C–H bond cleavage, in which the only requirement is to adjust the balance between the two different chemical bonds, namely C–H and C–C, to make the overall reaction thermodynamically feasible. In spite of such difficulties, there have been several reported catalytic reactions involving the cleavage of C–C bonds. In those reactions, the unfavorable catalytic C–C bond cleavage was achieved by embedding an energy-releasing step, such as hydrogenolysis, or, in the case of fragmentation reactions, by advancing the equilibrium through the removal of the co-product.[1,2]

This paper reviews the catalytic cleavage reactions of two specific classes of C–C bonds: 1) carbon–cyano (C–CN) bonds,

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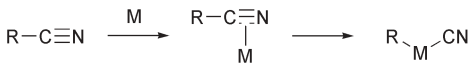
and 2) C–C triple bonds. In these reactions, the two predominant strategies—ring strain and chelation-assistance—are not utilized. Emphasis is placed on the (proposed) mechanism of the catalytic C–C bond cleavage, which could be helpful in the further development of the new reactions by both rational and inspirational design.

2. Catalytic cleavage of C–CN bonds

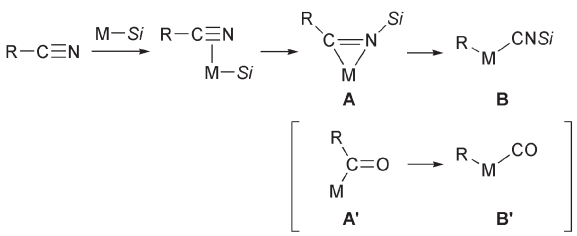
2.1 Mechanistic aspects

The organometallic reaction involving the cleavage of C–CN bonds was reported as early as 1971, in which the C–CN bond in tetracyanoethylene was oxidatively added to a Pt(0) center.[3] After that date, such oxidative additions have been reported to work with aryl, allyl and methyl cyanides as well as with numerous additional transition metal centers, such as Ni, Pd, and Pt (Scheme 1).[4]



Scheme 1 C–CN bond cleavage *via* oxidative addition.

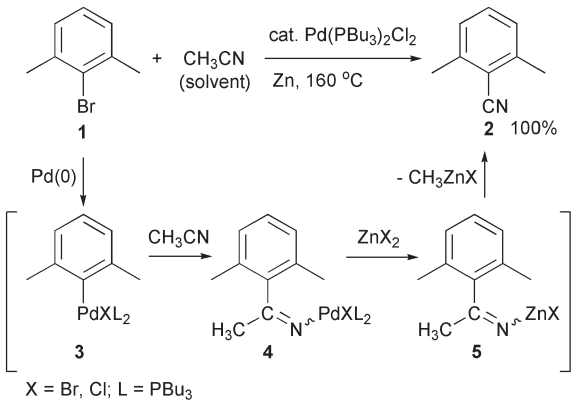
An alternative mechanism for the cleavage of C–CN bonds has recently been proposed by the research groups of Bergman and Brookhart. They reported that a certain Rh complex, containing a silyl ligand, mediates the C–CN bond cleavage as depicted in Scheme 2.[5,6] Thus, the insertion of a cyano group into the metal–silicon bond affords an η^2-iminoacyl complex **A**, followed by the migration of the R group to a metal center (deinsertion of silyl isocyanide) to induce the C–CN bond cleavage product **B**. An η^2-iminoacyl complex **A** was isolated and characterized by X-ray analysis. Nakazawa independently demonstrated that virtually the same mechanism was operating in the photoreaction of acetonitrile with a silyliron complex based on DFT calculation.[7,8] Although the mechanism involving deinsertion of silyl isocyanide was rather uncommon, the process is closely related to the decarbonylation of acyl complexes in which N–Si groups are replaced with oxygen atoms (**A′** → **B′**).



Scheme 2 C–CN bond cleavage *via* deinsertion of silyl isocyanide.

In accord with the advances in the stoichiometric C–CN bond cleavage reactions, several interesting catalytic reactions involving such a process have been accomplished. In the following sections (2.2 and 2.3), we will focus on the *catalytic* C–CN bond cleavage reactions classified by the above two mechanisms.

It should be noted that one catalysis in which a C–CN bond of alkyl cyanides was cleaved through neither of the



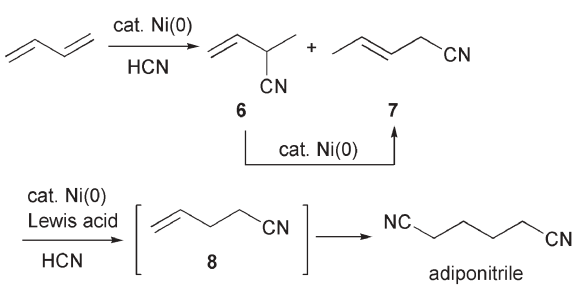
Scheme 3 Pd-catalyzed C–CN bond cleavage.

aforementioned two mechanisms has been reported (Scheme 3).[9] A cyano group was transferred from acetonitrile to bromoarenes in the presence of a palladium catalyst and zinc metal powder. On the basis of various stoichiometric experiments, the following mechanism was proposed: 1) addition of aryl palladium **3** to acetonitrile, forming an iminyl palladium complex **4**, 2) transmetalation, affording iminyl zinc species **5**, and 3) β-methyl elimination, producing a nitrile **2** and CH_3ZnX.

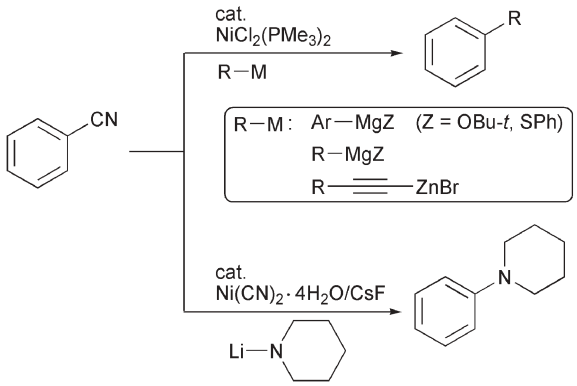
2.2 Catalytic cleavage *via* oxidative addition

It has been proposed that most of the catalytic C–CN bond cleavage reactions reported to date proceed through an oxidative addition mechanism. The earliest example can be seen in the Dupont's production of adiponitirile by the Ni(0)-catalyzed two-step double hydrocyanation of 1,3-butadiene (Scheme 4). The first addition of HCN produced a kinetic mixture of the undesired branched isomer **6** and the desired linear isomer **7**. The branched nitrile **6** was isomerized *in situ* to the linear isomer **7** by the reversible C–CN bond cleavage/formation reaction, followed by the catalytic addition of the second HCN, leading to adiponitirile. The isomerization step (**6** → **7**) has also been studied independently. In those studies, a π-allyl nickel cyanide complex, formed *via* the C–CN bond oxidative addition, has been invoked as an intermediate.[10]

A series of catalytic cross-couplings of aryl cyanides with organometallic reagents has been reported by Miller (Scheme 5).[11] Aryl cyanides can serve as pseudo-halides in these cross-couplings, although the bond dissociation energy



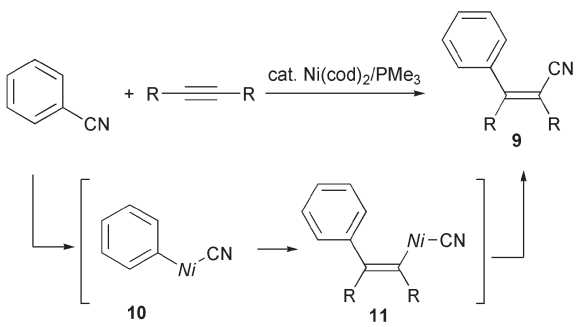
Scheme 4 Ni(0)-catalyzed hydrocyanation of butadiene.



Scheme 5 Ni-catalyzed cross-couplings and amination of aryl cyanides.

of aryl cyanides is larger than that of halides (Ar–CN: ~130 kcal mol^{-1}, Ar–Br: ~80 kcal mol^{-1}, Ar–Cl: ~100 kcal mol^{-1}). While palladium-based catalysts are among the most effective for the cross-coupling reactions of aryl halides, the reactions for aryl cyanides can be catalyzed only by nickel complexes, highlighting the outstanding activity of a low-valent nickel species, generated *in situ*, to mediate the oxidative addition of C–CN bonds. In the cross-coupling reaction with Grignard reagents, prior treatment of Grignard reagents with either a bulky alkoxide or a thiolate effectively suppressed the formation of imine side products. The Ni-catalyzed protocol can also be applied to alkynylation of aryl cyanides by the use of alkynylzinc reagents as a nucleophile.[12] In addition to C–C bond forming reactions, aryl cyanides can serve as a good substrate for catalytic amination.[13]

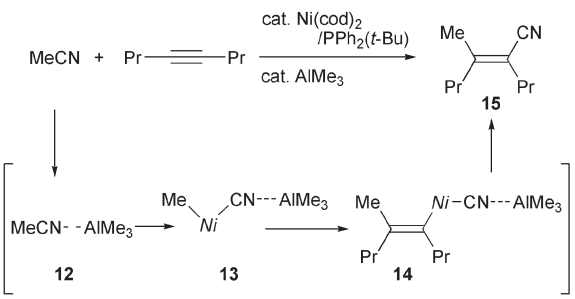
The characteristic activity of low-valent nickel complexes toward the oxidative addition of C–CN bonds has been further applied to new catalysis by Nakao and Hiyama. They reported that an insertion of alkyne into an aromatic C–CN bond, in other words, arylcyanation of alkynes, can be catalyzed by a nickel complex (Scheme 6).[14] The addition of an arylnickel complex **10**, formed *via* the oxidative addition of aryl cyanide, onto an alkyne affords an alkenylnickel complex **11**, which then liberates the α,β-unsaturated nitrile by reductive elimination. The choice of ligand is critical for this type of reaction to occur. The less hindered and electron-rich PMe_3 is an optimal ligand in arylcyanation reactions, as was observed in the cross-coupling reactions shown above (Scheme 5). Interestingly, Louie reported that the use of N-heterocyclic carbenes as a



Scheme 6 Ni-catalyzed arylcyanation of alkynes.

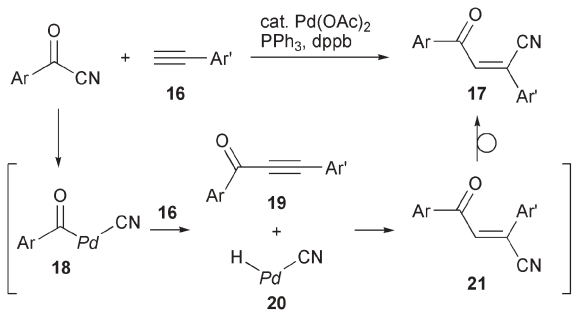
ligand completely changes the reaction path to [2 + 2 + 2] cycloaddition, which leads to pyridine derivatives.[15] In addition to alkynes, norbornene and norbornadiene can be inserted into C–CN bonds through this catalysis.[16] Moreover, C–CN bonds in allyl cyanides can be added to alkynes *via* a π-allylnickel intermediate.[17]

To this point, our review has concentrated on the catalytic reactions involving the oxidative addition of C–CN bonds in aryl and allyl cyanides. The utilization of C–CN bonds in *alkyl* cyanides for catalytic reactions represents a difficult task, due not only to the thermodynamic stability of the $C(sp^3)$–CN bond but also to the susceptibility of the intermediate, an alkylmetal cyanide complex, to β-hydride elimination. Recently, Nakao and Hiyama reported that the scope of the Ni-catalyzed arylcyanation reaction (Scheme 6) can be expanded dramatically by the presence of a Lewis acid co-catalyst.[18] Under the improved conditions, the C–CN bond in the acetonitrile can be added across the alkynes (Scheme 7). Reportedly, in the stoichiometric systems involving a cyano group, both the oxidative addition[19] and reductive elimination,[20] are accelerated by the coordination of the cyano group to Lewis acids. Thus, a similar effect must be operating in the catalytic carbocyanation reaction.

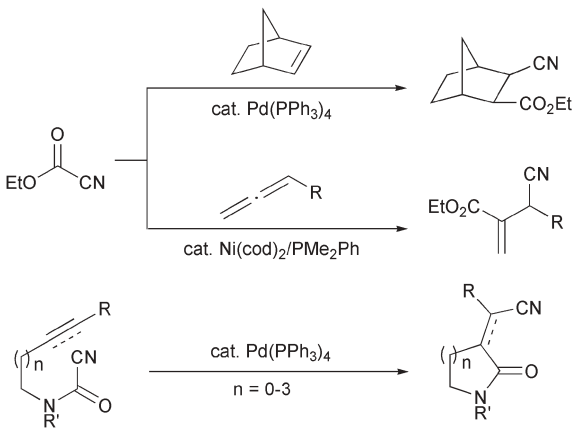


Scheme 7 Ni-catalyzed carbocyanation of alkynes in the presence of Lewis acid.

It is known that the C–C bonds between a carbonyl carbon and the α-carbon can be cleaved by transition metals more facilely than can other C–C bonds, due to their polarized character.[1,2] Similarly, the facile oxidative addition can be expected for the C–CN bonds in acyl cyanides or cyanoformates, when compared with the C–CN bonds in aryl cyanides. Indeed, several catalytic reactions involving this special class of C–CN bonds have been reported. One of the earliest examples of such reactions was the decarbonylation of acyl cyanides, catalyzed by Rh[21] and Pd.[22] The catalytic insertion of alkynes into a C–CN bond in acyl cyanides was reported by Nozaki and Takaya (Scheme 8).[23] A mechanism different from the related Ni-catalyzed arylcyanation (Scheme 6) was proposed. The oxidative addition of a C(=O)–CN bond to a palladium center gives a acylpalladium intermediate **18**, which reacts with a terminal alkyne **16** to give an alkynyl ketone **19** and a palladium hydride **20**. Subsequently, hydrocyanation of the alkyne **19** by a palladium complex **20** affords *E*-alkene **21**, which isomerizes to a thermodynamically stable *Z*-isomer **17**. In accordance with the proposed mechanism, internal alkynes cannot be applied to this reaction.



Scheme 8 Pd-catalyzed formal insertion of alkynes into a C–CN bond in acylcyanides.

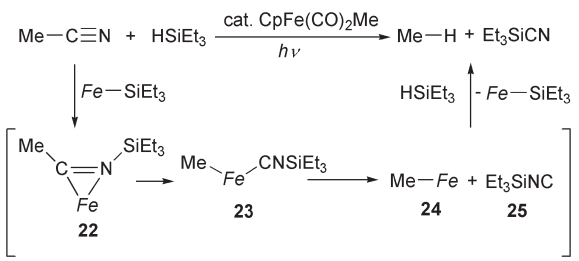


Scheme 9 Catalytic additions of C(=O)–CN bonds to various unsaturated molecules.

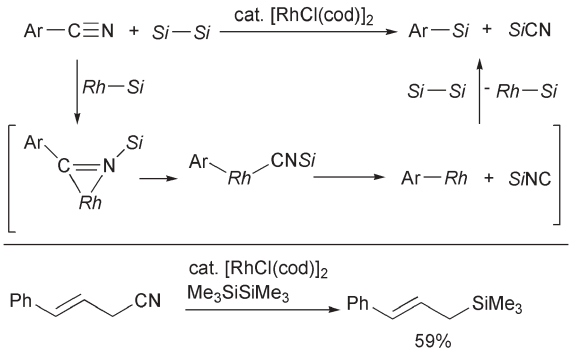
The carbometallation of the palladium complexes formed through the oxidative addition of the C(=O)–CN bonds proceeds when norbornene derivatives[24] or 1,2-dienes[25] are employed in place of the terminal alkynes (Scheme 9). The catalytic addition of the C(=O)–CN bonds across intramolecular alkynes and alkenes has been reported.[26]

2.2 Catalytic cleavage *via* deinsertion of silyl isocyanide

Only two catalytic C–CN bond cleavage reactions have been proposed to proceed through an alternative mechanism, namely deinsertion of silyl isocyanide. Nakazawa reported the iron-catalyzed reaction of acetonitrile with hydrosilane under photoirradiation conditions, leading to the formation of CH_4 and silyl cyanide (Scheme 10).[27] That study identified a silyliron complex as an active catalytic species that, once added



Scheme 10 Fe-catalyzed C–CN bond cleavage with hydrosilanes.



Scheme 11 Rh-catalyzed C–CN bond cleavage with disilanes.

to a cyano group, forms **22**, followed by the deinsertion of silyl isocyanide to afford a methyliron complex **23**. The dissociation of silyl isocyanide **25** from an iron center generated the coordinatively unsaturated complex **24**, which reacted with hydrosilane to furnish CH_4 and thus regenerated a silyliron complex—an active species. The dissociated silyl isocyanide **25** was isomerized into thermodynamically stable silyl cyanide. The coproduced silyl cyanide was utilized for the subsequent iron-catalyzed silylcyanation of carbonyl compounds in one-pot.[28] Aryl cyanides also served as good substrates in this catalysis, in which a cyano group was exchanged for a hydrogen atom.

Our group has reported another example of a catalytic C–CN bond cleavage through deinserion of silyl isocyanide. The reaction of aryl cyanides with disilanes in the presence of a rhodium catalyst resulted in the cleavage of C–CN and Si–Si bonds, which yielded the arylsilanes and silyl cyanide (Scheme 11).[29] A variety of functional groups, such as esters, ethers, amines, and boronic esters, are compatible with this catalysis. In addition, alkenyl and allyl cyanides can be silylated through this catalysis. It is interesting to note that the nickel-based catalyst, which can be expected to promote a facile oxidative addition of C–CN bonds, was totally inactive in this reaction.

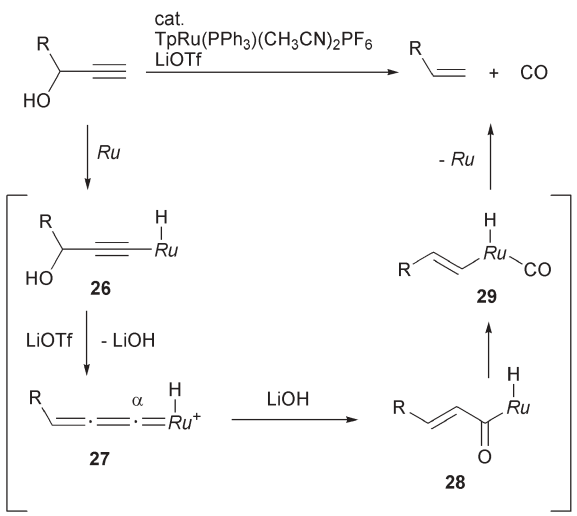
3. Catalytic cleavage of carbon–carbon triple bonds

Among common chemical bonds, there is little doubt that the cleavage of a C–C triple bond is one of the most difficult tasks to achieve owing to its extraordinarily large bond dissociation energy (>200 kcal mol^{-1}). Transition-metal-mediated approaches are promising since the alkyne moiety is an excellent ligand for transition metals and the alkynes bound to a metal center have been known to exhibit a variety of reactivities. However, despite intensive studies in stoichiometric systems, catalytic reactions involving the cleavage of a C–C triple bond have been limited. Such catalytic reactions can be classified into three categories: 1) alkyne metathesis,[30] 2) tandem reactions that involve the addition of an external organic compound to the alkyne moiety and the subsequent fragmentation reaction, such as retro-Mannich and retro-Diels–Alder reactions,[2] and 3) reactions that do not require external organic promoters. Since the first two categories have been recently reviewed, this review will focus on the catalytic reactions of the third category. In this type of reaction,

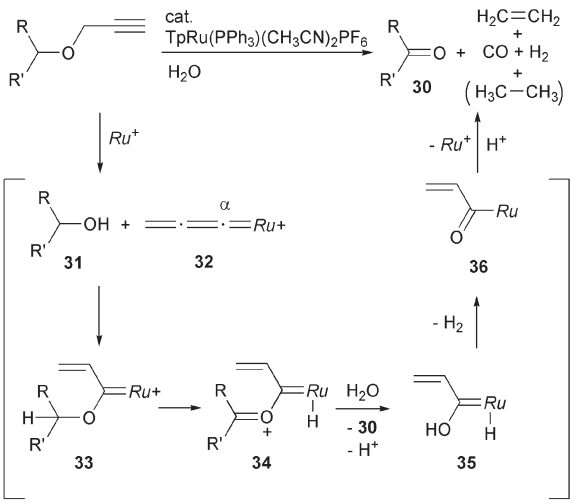
establishing the process to convert a C–C triple bond into a more reactive species by a metal-catalyzed isomerization is critical.

3.1 Catalytic fragmentation of alkynes containing OH and related functionalities

It has been well-recognized that propargyl alcohols can form a reactive allenylidene intermediate ($M{=}C{=}C{=}CR_2$) *via* dehydration with the aid of certain transition metal complexes.[31] R.-S. Liu has utilized the formation of an allenylidene intermediate for the catalytic cleavage of a carbon–carbon triple bond of propargyl alcohols. In the presence of a catalytic amount of a ruthenium complex and LiOTf, propargyl alcohols are split into alkenes and carbon monoxide, the carbon atom of which is derived from the terminal carbon of the alkyne moiety (Scheme 12).[32] They proposed a mechanism involving an acylruthenium species, such as **28**, on the basis of related stoichiometric reactions. Thus, the proton migration of the initially formed π-alkyne complex affords the η^1-alkynyl hydride species **26**, which was then ionized *via* the elimination of an OH group with the assistance of a Lewis acid co-catalyst, generating the allenylidene intermediate **27**. Subsequently, the electrophilic C_α carbon of the allenylidene complex **27** was attacked by a hydroxide ion to form the ruthenium-acyl species **28**, which undergoes deinsertion of carbon monoxide to induce the cleavage of the C–C bond derived from the alkyne moiety. The net 1,3-shift of the oxygen functionality *via* an allenylidene intermediate was further employed for the catalytic fragmentation of propargyl ethers into ketones, ethylene, carbon monoxide, and hydrogen (Scheme 13).[33] Similar to the mechanism shown in Scheme 12, the allenylidene intermediate **32** was generated from propargyl ethers by the elimination of alcohol **31**, which added to the C_α carbon of **32**, yielding a carbene complex **33**. The hydride migration and substitution by water provide a ketone **30**, hydrogen, and an acyl complex **36**, which finally gave ethylene and carbon monoxide by decarbonylation. The common strategy for C–C triple bond cleavage in these reactions is the following: 1) the conversion of the C–C triple bond into a C(=O)–C single bond in an acyl complex *via* the transposition of an oxygen functionality at the propargylic position, and 2) the decarbonylation of the acyl complex cleaves a C(=O)–C bond. Although the strategy is highly interesting from a mechanistic point of view, its major limitation for the time-being is its inapplicability to internal alkynes.

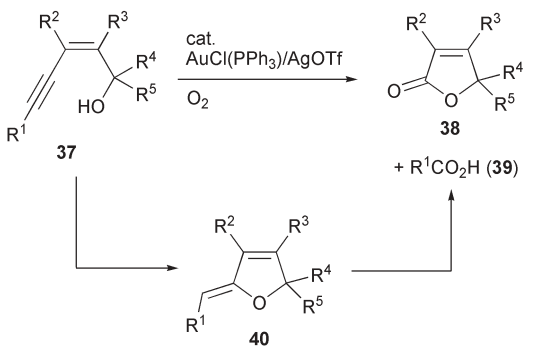


Scheme 12 Ru-catalyzed cleavage of a carbon–carbon triple bonds of ethynyl alcohols.



Scheme 13 Ru-catalyzed cleavage of a carbon–carbon triple bonds of propargyl ethers.

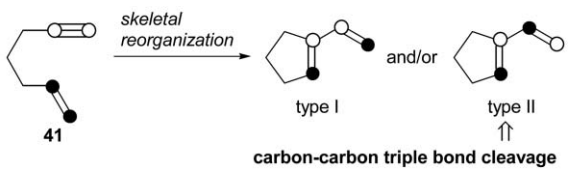
The gold-catalyzed cascade process for the net oxidative cleavage of a carbon–carbon triple bond has been devised by Y. Liu (Scheme 14).[34] The 5-*exo* cyclization of alkynic alcohol **37** initially proceeds by gold catalysis, converting the alkyne moiety into an exocyclic double bond. This electron-rich double bond in **40** is now susceptible to the oxidative cleavage reaction catalyzed by the same gold complex under an oxygen atmosphere, furnishing a butenolide **38** and a carboxylic acid **39**. It should be noted that normal olefins, such as 1-decene and styrene, cannot be oxidized under these conditions, whereas enol ethers do react, indicating that the second process of this cascade reaction requires an electron-rich alkene moiety. Involvement of a radical species is implied based on the observation that the reaction is completely suppressed in the presence of a radical scavenger.



Scheme 14 Au-catalyzed cascade cyclization/oxidative cleavage of (*Z*)-enynols.

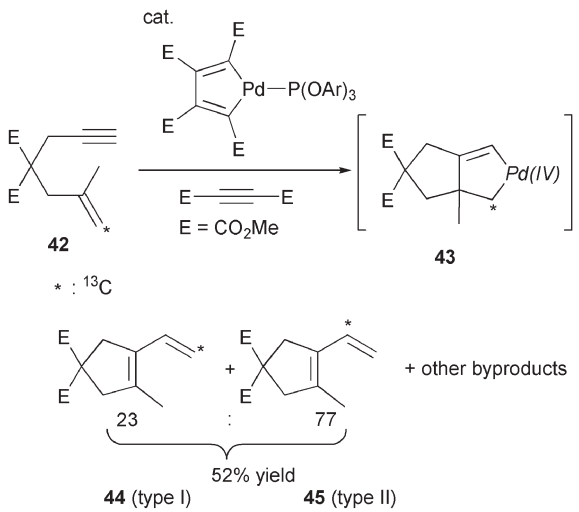
3.2 Catalytic skeletal reorganization of enynes

Catalytic cycloisomerization of enynes to 1-alkenylcyclopentene, particularly its mechanistic diversity, have been the subject of intensive studies. A representative class of the catalysts for this process is electrophilic transition metal salts, such as Pt and Au, which trigger cycloisomerization by activating the alkyne moiety electrophilically.[35] Through this catalytic cycloisomerization, or more appropriately skeletal reorganization, enyne **41** can be isomerized into two types of products (Scheme 15). Type I is the product in which the original alkene moiety is cleaved and added to the alkyne moiety of **41**. The formally same product is obtained in the enyne-metathesis.[36] On the other hand, type II is the product in which both double and triple bonds in **41** are cleaved and the terminal carbon atom of the alkene moiety in **41** is inserted into the alkyne C–C bond. It is important to note that these two types of products can be distinguished only when starting from enynes bearing a substituent at the terminal of either an alkyne or an alkene moiety. Despite the growing interest in skeletal reorganization processes, most reports focus on the formation of the type I product, and the observation of the type II product is limited. This section is an overview of the formation of the type II product.

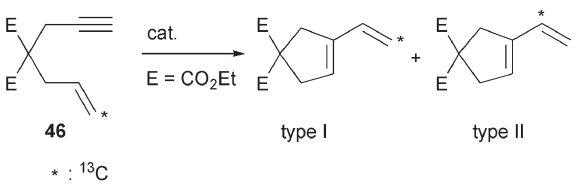


Scheme 15 Cycloisomerization of enynes into 1-alkenylcycloalkene.

The formation of the type II product was first observed by Trost in a palladium-catalyzed system (Scheme 16).[37] The skeletal reorganization of ^{13}C-labelled enyne **42** afforded the unexpectedly labelled **45** as a major product in addition to the type I product **44**. The palladacyclopentene **43** has been proposed as the common intermediate for the formation of **44** and **45**.



Scheme 16 Pd-catalyzed skeletal reorganization of enynes.



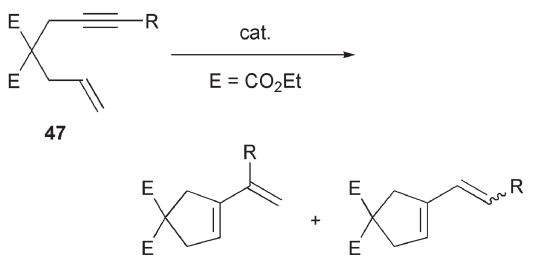
catalyst	yield	type I : type II
$[RuCl_2(CO)_3]_2$ / CO (1 atm)	81%	7:93
$PtCl_2$	53%	6:94
$PtCl_4$	57%	7:93
$[IrCl(CO)_3]_n$	83%	21:79
$Rh_2(O_2CCF_3)_4$	81%	39:61
$AuCl_3$	42%	40:60

Scheme 17 Skeletal reorganization of enynes.

We have discovered that the skeletal reorganization of enynes is catalyzed by electrophilic metal salts, such as Ru(II),[38] and Pt(II).[39] Although, with most enynes, the type I product is obtained exclusively. Labelling studies revealed that the type II product was predominantly formed with a variety of metal salts when an enyne bearing no substituents, neither at the alkyne nor at the alkene terminal, namely **46**, was employed (Scheme 17).[40]

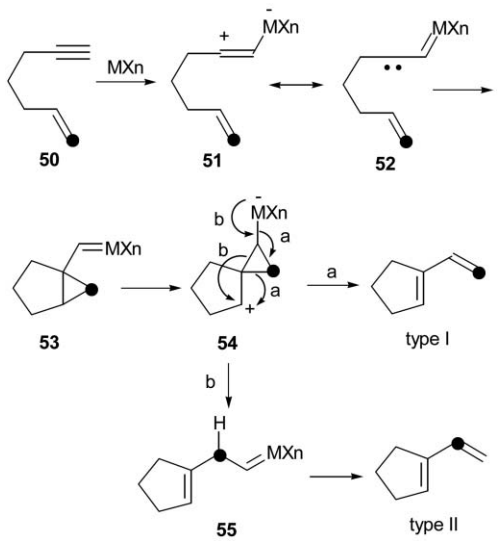
Moreover, in sharp contrast to the Trost's system,[37] enynes containing an ester group at the alkyne terminus furnished the type II product **49** selectively,[39] indicating that a different mechanism was likely to be involved in this system (Scheme 18, R = CO_2Et). While the enynes bearing a methyl group at the alkyne terminus predominantly afforded the type I product **48** with $PtCl_2$, the selectivity is reversed by utilizing the cationic Pt,[41] $PtCl_4$[42] or Au[43] complexes (Scheme 18, R = Me).

The possible mechanism that can explain the formation of both type I and type II products is shown in Scheme 19. The alkyne moiety of enynes is electrophilically activated by transition metal salts to form a vinyl cation intermediate **51**, which can also be drawn as a carbene carbenoid complex **52**.



cat.	R	total yield	**48**:**49**
$PtCl_2$	CO_2Et	80%	0:100
$PtCl_2$	Me	84%	89:11
$[Pt(dppp)(PhCN)_2](BF_4)_2$	Me	74%	0:100
$PtCl_4$	Me	66%	10:90
$Au(PPh_3)Cl/AgSbF_6$	Me	95%	0:100

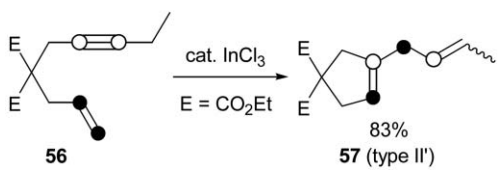
Scheme 18 Pt-catalyzed skeletal reorganization of enynes.



Scheme 19 Possible mechanism for the Pt- and Ru-catalyzed skeletal reorganization of enynes.

The attack by an intramolecular alkene toward a cationic center affords a cyclopropyl carbenoid intermediate **53**.[44] Although the intermediate **51** (and **52**) is shown to highlight the nature of the alkyne moiety electrophilically activated by metal salts, direct formation of **53** from **50** is also possible.[45] The intermediate **53** then isomerizes into a spiro complex **54**, which leads to either a type I or type II product depending on the orientation of the cyclopropane ring opening. When the C–C bond between a spiro carbon and a carbon derived from the alkene terminal is cleaved (path a), a type I product is formed. On the other hand, the cleavage of the bond between a spiro carbon and a carbon α to a metal center affords a carbenoid intermediate **55**,[46] which finally furnishes the type II product *via* α-C-H insertion.

We have also reported that the skeletal reorganization of enynes can be catalyzed also by main group metal halides, such as $GaCl_3$[47] and $InCl_3$,[48] which have been reported to have a high affinity toward a carbon–carbon triple bond.[49] With these catalysts, the major product is type I when enynes bearing no substituents at the alkyne terminal are employed. This is in sharp contrast to the reactions catalyzed by transition metal halides (Scheme 17). On the other hand, enynes containing an alkyl substituent at the alkyne terminal, such as **56**, afforded an unexpected 1,4-diene **57** as the sole product in the presence of an $InCl_3$ catalyst (Scheme 20). Labelling studies unambiguously established that the arrangement of the carbon atoms was identical to the type II product, while the type II contains a 1,3-diene moiety.



Scheme 20 $InCl_3$-catalyzed skeletal reorganization of enynes.

Conclusions

In this review, we have presented an overview of catalytic reactions involving the cleavage of two types of C–C bonds: a C–CN bond and a C–C triple bond. Those C–C bonds can be cleaved catalytically in the absence of ring strain and chelation assistance, which are the predominant strategies for C–C bond activation by transition metal complexes. In the catalytic C–CN bond cleavage reactions, two different mechanisms, namely oxidative addition and deinsertion of silyl isocyanide, can be employed. In both cases, a variety of reactivities of the postulated organometallic intermediates allowed the development of new reactions. Catalytic cleavage reactions of a C–C triple bond can be accomplished *via* unique organometallic species, such as allenylidene and cyclopropyl carbenoid intermediates. As discussed in this review, diverse mechanisms are involved even in the cleavage of the two specific classes of C–C bonds. Further development of new C–C bond cleavage reactions can thus be expected by exploring the new reactivity of organometallic intermediates shown in this review. Moreover, opportunities abound for discoveries of catalytic reactions involving a completely new elemental organometallic process or new intermediates. We hope this review stimulates the advancement of studies in this fascinating and nascent field.

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