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Transformations of X (C, O, N)-CN Bonds: Cases of Selective X (C, O, N)-C Activation**

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Abstract

Activation of C-C, C-N, and C-O bonds has in recent decades been recognized as a valuable strategic objective. While considerable progress has been achieved, many of the more challenging issues, *e.g*., regioselective activation of specific C-X (C, O, N) bonds, chemoselective cleavage of $C_{(sp3)}$-X bonds, enantioselective activation and even the successful application of solid catalysts in such transformations remain elusive. The research disclosed herein summarize recent advances in C-X bond cleavages, including regioselective processes, although the carbon is activated in the form of a cyano group.

Keywords

C-CN bond; O-CN bond; N-CN bond; cyanation; silicon reagent

Starting as early as the 1960s, C-H activation has been a vibrant topic.[1] In contrast, comparable C-C bond activation, while thermodynamically permitted, has been largely elusive.[2] The higher bond energy and elevated kinetic barriers compared to C-H activation renders this pathway substantially refractory towards transition metal complexes.[2a] Meanwhile, C-CN bond activation[3] has been realized using several transition metal complexes which can overcome the relatively high bond dissociation energy due to the unique nature of the cyano group (*e.g*., electron-withdrawing, polarized bond, high affinity for some metals).[4] Traditionally, C-CN bonds were cleaved using metals such as Feand Rh in tactical combination with organic silicon reagents or metal-Lewis acid bifunctional catalysts.[5] Most recently, Ni(0) and Pd(0) mediated C-CN bonds cleavage were reported. Related O-CN bond activations[6] have been realized in only a few cases while N-CN bond activation[7] is even rarer. Considering the paramount role of the elements such as nitrogen, oxygen and carbon in organic chemistry, moreover, the broad existence of cyano groups in natural (*e.g*., Cyanocycline A, Dnacin A1, Halimedin, Lahadinines A, et al.) and/ or medical molecules (*e.g*.,PPARgamma-active triterpenoid, 2-cyano-3,12-dioxooleana-1,9-dien-28-oic acid), along with the versatile application of cyano group towards spectacular precursor to vast functionalized groups, *viz*., (i) amine; (ii) amide; (iii) acid; (iv) aldehyde; (v) ester; (vi) ketone; (vii) thioamide; (viii) hydroxyimidamide et al, reactions involved with such transformation can be of high importance. Additionally, cyano also can serve as a directing group, firstly introduce a functionalized group on the *ortho*-position, subsequently was converted into other group, all these aspects contribute to the ceaselessly investigation of cyano-containing reaction in organic synthesis. Thus, reactions via C-CN, O-CN and N-CN

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Dedication

bonds activation whether single process and/ or domino reaction make it remarkable, nevertheless the interesting structure of those products (*e.g.*, dihydrobenzofuran) obtained in such transformations.

Actually, the related bonds dissociation energies are summarized in Table 1, which intuitively showed the strength of bonds between different atoms such as C-H,C-C, C-O and C-N et al. The facts directly indicate the inert nature of these transformations in the reaction.

In a recent publication, Chatani and co-workers reported a rhodium catalyzed C-CN bond cleavage and subsequently new C-B bond generation.[8] The extraordinary synthetic versatility of C-B bonds[9] put a spotlight on this challenging transformation.

In 1971, the first example of oxidative addition to a C–CN bond was observed.[4l] In 2002, Brookhart and co-workers disclosed Rh (III) can activate C-CN bonds.[3x,y] The first example of carbo cyanation via cleavage of a C-CN bond was realized by Hiyama et al a few years later.[3v] Subsequently, Chatani,[3r]Hiyama[3e,g,q,u] and Jacobsen[3f,n] et al reported several key results for the generation of C-Si, C-H,C-C bonds, respectively, via C-CN activation based on the preceding results from Hiyama. Finally, C-CN bond cleavage resulting in the formation of C-B bond was realized (Scheme 1).[8]

The mild reaction conditions allow broad substrate application (Scheme 2). Notably, electron-rich aryl, -deficient aryl and heteroaryl nitriles as well as alkenyl and benzyl nitriles efficiently proceed along the desired pathway utilizing di-boron reagents to afford the corresponding boron compounds. Impressively, Chatani and co-workers also reported several complex substrates possessing relatively sensitive functional groups such as chiral α-methyl esters and even an aryl chloride. These observations should expand the usage of this methodology in organic synthesis and provide a new strategy for the construction of complex boronic acid derivatives wherein a cyano group can be utilized as a boronic ester equivalent. To date, the transformation can be of high importance. With vast functionalized group tolerance, chemists may change their synthetic strategies, *e.g.*, serving as the directing group, cyano group firstly introduce ortho position functionalization, subsequently cyano group was transferred to other one (*e.g.*, CF_3) via boronic intermediate. Future application of such one will definitely spectacular among synthesis community.

The first systematic study of the cleavage of the C-CN bond was initiated in the 60s by Bergman and co-workers who described the C(carbonyl)-CN bond disconnection reaction.[10] Mechanistic studies of such metal-catalyzed C-CN bond cleavage reactions indicated that nitriles coordinate to metals either in an η^1- or η^2-fashion (Scheme 3).[3o,5] In one possible pathway, the transition metal oxidatively inserts into the C-CN bond affording a R (alkyl or aryl)-metal-cyano reactive species (Scheme 3, pathway A). An alternative (Scheme 3, pathway B) relies upon the assistance of a silicon reagent; the newly generated metal-silyl species mediates the C-CN bond cleavage with release of silyl cyanide. Generally, Pd(0) and Ni(0) and related metals together with a Lewis acid (*e.g.*,BPh_3, Et_2AlCl) catalyse cyano activation reactions via pathway A, while most of other metal catalyzed C-CN cleavage reactions proceeded through the later pathway B.[11]

These authors[8] invoke a similar provisional mechanistic hypothesis as shown in pathway B (Scheme 4) for the borylation of aryl cyanides. The in situ generated rhodium complex **4** reacts with aryl cyanide **5** to generate intermediate **6** by the insertion into the Rh-B bond, subsequent release of boronyl cyanide **7** resulting in the aryl-Rh complex **8**. The latter complex reacts again with di-boron reagent **2** yielding aryl boronic ester **9** along with the intermediate **4** thus propagating the catalytic cycle.

All the cases presented above are C-CN bond activation reactions. Although other element-cyano bond cleavages, such as silyl-cyano,[12] germyl-cyano,[13] stannyl-cyano,[14] boryl-cyano,[15] sulfur-cyano,[16] and bromo-cyano[17] have been achieved, a useful synthetic transformation of oxy-cyano has not been reported yet.[6] In 2012, Nakao and co-workers disclosed palladium and triphenylborane catalyzed the intramolecular. oxycyanation of alkenes via the cleavage of O-CN bonds and the subsequent insertion of double bonds.[6a] This reaction illustrates the cyanofuctionalization of a double bond through cleavage of an oxygen-cyano bond, which is rare till now. Moreover, this transformation allowed intramolecular oxycyantion of alkenes, to provide substituted dihydrobenzofurans having both a tetra-substituted carbon and cyano functionality for the first time(Scheme 5).[18] Preliminary mechanistic studies supported a process similar to pathway B wherein a LA (BPh_3) mimics the silicon reagent. The Lewis acid catalyst is crucial for the oxidative addition to O−CN bonds whereas it has also been shown to promote $C_{(sp3)}$−CN bond-forming reductive elimination from palladium(II) through coordination of a cyano group to the Lewis acid. As benzofuran derivatives broadly existing in natural and medical chemistry and the versatile manipulation of cyano group (precursor to amine, amide, acid, et al.), the methodology disclosed herein can construct benzofuran derivatives and functionalized cyano group in one pot. Considering the demand of atom-economy in modern chemistry, this will attract great interest in the future.

As for N-CN bond activation, this transformation is even rarer.[7] In 2011, Beller et al presented an interesting example of a N-CN cleavage reaction as showed in Scheme 6.[7d] Rhodium complexes catalyzed activated N-CN bond cleavage, followed by transformation of an aryl boronic acid to aryl cyanide. It should be appreciated that *N*-cyano-*N*phenyl-*p*-toluenesulfonamides are unique cyanation reagents, *i.e*., the N-CN bond is activated both by Ts and phenyl groups. The authors postulated a similar mechanism as pathway B, *viz*., (i) aryl boronic acid transmetallation by the rhodium(I) complex, (ii) coordination with the N-CN, (iii) aryl migration from rhodium to carbon, and finally (iv) reductive elimination connecting the cyano to the aryl. This is the first example of a rhodium-catalyzed cyanation of aryl and alkenyl boronic acids via N-CN bond activation. Notably, considering the importance of cyano group in organic chemistry, this pioneering cyanation methodology presented herein will be synthesis useful, not only because the non-toxic property of cyanation reagent **13**, but also the rapid introduction of cyano group to aryl and styrenyl molecules (*e.g*., malloapeltine, ricinidine).

In 2011, Wang and co-worker observed that metals such as Pd(0) or Rh(I) can activate a N-CN bond in an intramolecular process to provide a series of 3-arylacrylonitriles from styrenes.[7a] Substitution on the arenes and α -position of the styrenes was well tolerated. This was the first example of an intramolecular cyanation of a $C_{(sp2)}$ through N-CN bond cleavage. While mechanistic studies are still under the way, established precedent suggests this transformation follows a course similar to pathway A in Scheme 3; specifically, (i) oxidative addition of the rhodium complex into the N-CN bond, (ii) double bond insertion into the newly generated N-Rh bond, and (iii) β-elimination to regenerate the reactive Rh(I) allowing the catalytic cycle to continue. This case indicated that intra-molecular cyantion of styrene can be realized through the rarely reported N-CN bond cleavage strategy under related mild reaction condition. This will add one new type of N-C bond activation and will inspire future discovery of bond-bond activation. Moreover, the stereo-specific 3-arylacrylonitriles products obtained in this transformation are also useful intermediates, which will expand the application scope of such transformation.

Most recently, Liu and Fu reported an interesting and potentially highly useful intermolecular cyanation reaction[7e] using the previously reported Beller cyanation reagent, *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide(NCTS). This reaction allows intramolecular

cyanation of arenes via C-H bond activation mediated by rhodium catalyzed N-CN bond cleavage. A wide variety of aryl substituents and even heterocycles are tolerated and the regioselectivity can be controlled by many common directing groups. A kinetic isotope (KIE) experiment revealed the transformation is typical of Rh catalyzed C−H activation processes, followed sequentially by coordination with the N-CN moiety and elimination to provide the cyanated products. Thus these authors have developed an unprecedented and practical Rh catalyzed C−H cyanation reaction that uses less toxic and the readily available NCTS as the cyanation reagent. Although the cyanation reagent (**13, NCTS**) was firstly introduced by Beller and co-workers, Liu and Fu's work disclosed herein made it more practicable and useful. That is, synthesis was not only restricted to manipulation of boronic derivatives, but also was applied in the transformation of C-H activation with the assistance of DGs. In the future, chemists may introduce a cyano group to any molecules with the assisting of directing groups at the late stage. As cyano group broadly exist in natural (*e.g.*, cyanopuupehenone, benthocyanin C, Ambiguinine G nitrile, et al.) and/ or medical moleculars and is readily transferred into other functionalized groups, this will definitely be a powerful tool in organic synthesis.

In classical organic chemistry, the emphasis was on bond formation, especially C-C and to a lesser extent C-N and C-O. Conversely, activation of C-C, C-N, and C-O bonds has in recent decades been recognized as a valuable strategic objective. While considerable progress has been achieved, many of the more challenging issues, *e.g.*, regioselective activation of specific C-X (C, O, N) bonds, chemoselective cleavage of $C_{(sp3)}$-X bonds, enantioselective activation and even the successful application of solid catalysts in such transformations remain elusive. The research disclosed herein summarize recent advances in C-X bond cleavages, including regioselective processes, although the carbon is activated in the form of a cyano group. We believe the results disclosed herein will attract vast interest and lead to new synthetic applications in the future.

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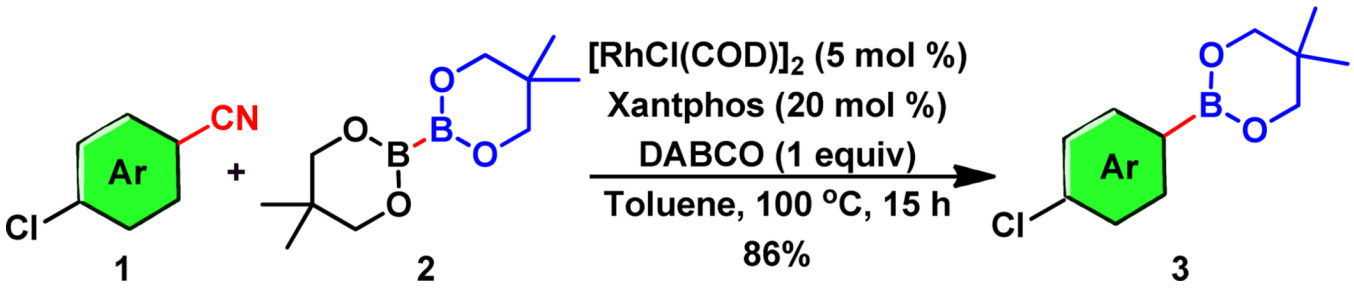
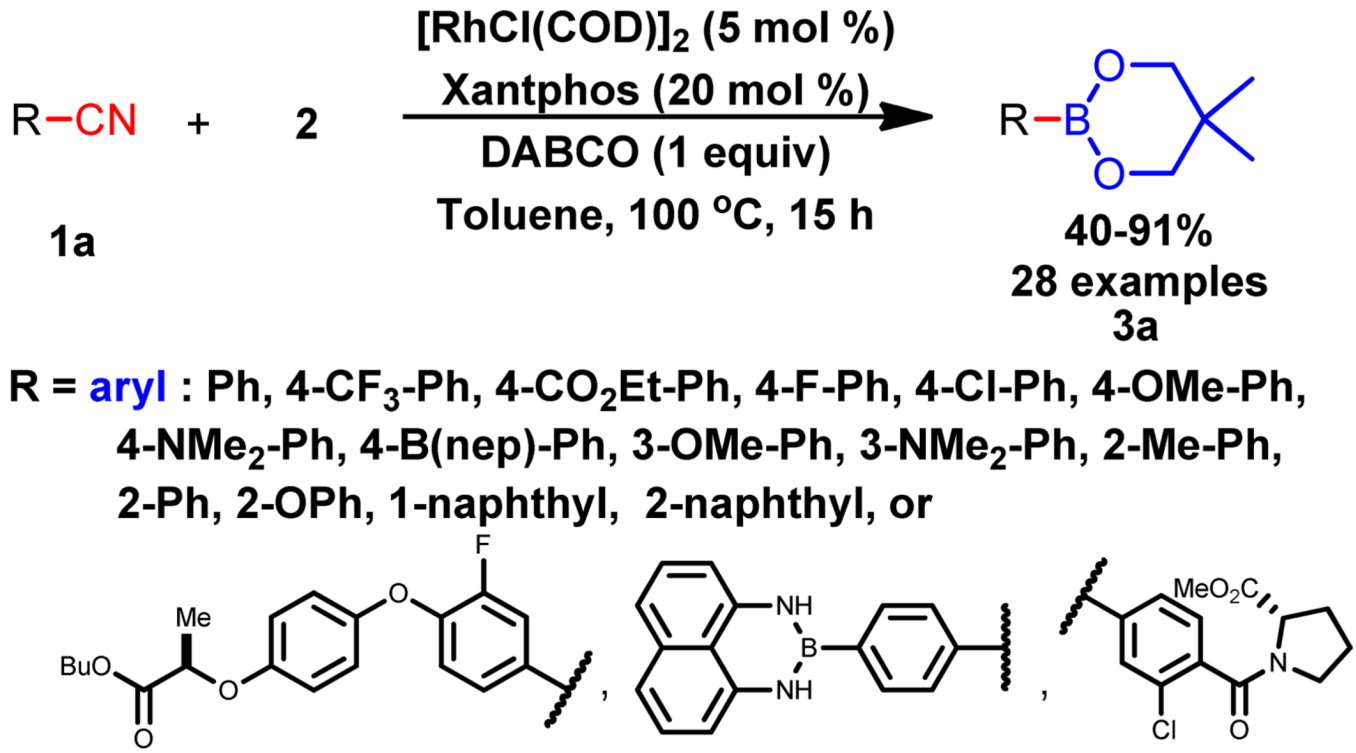
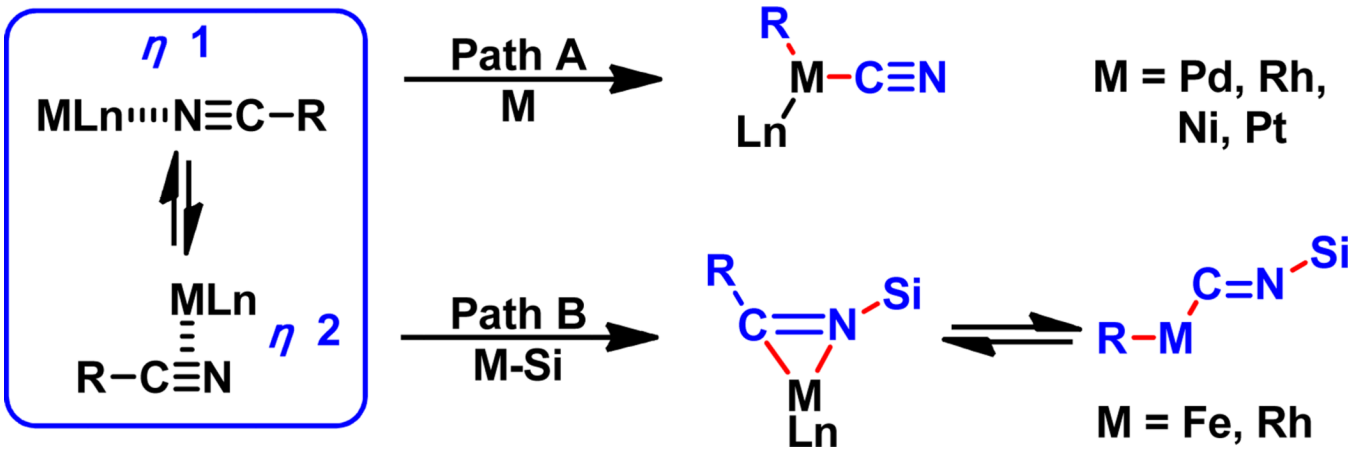


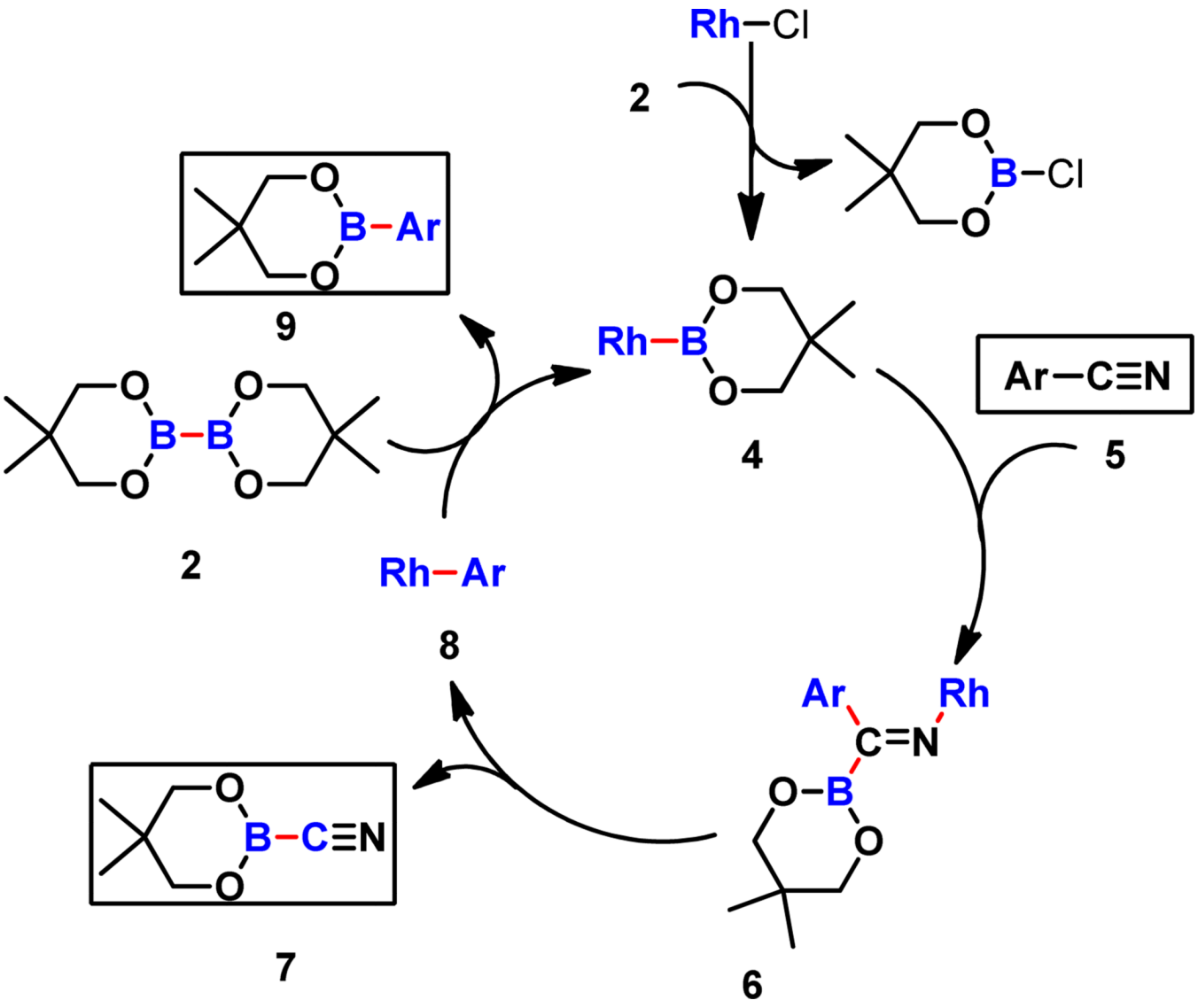
Scheme 1.
Rhodium catalyzed C($_{sp2}$)-CN to C($_{sp2}$)-B replacement.



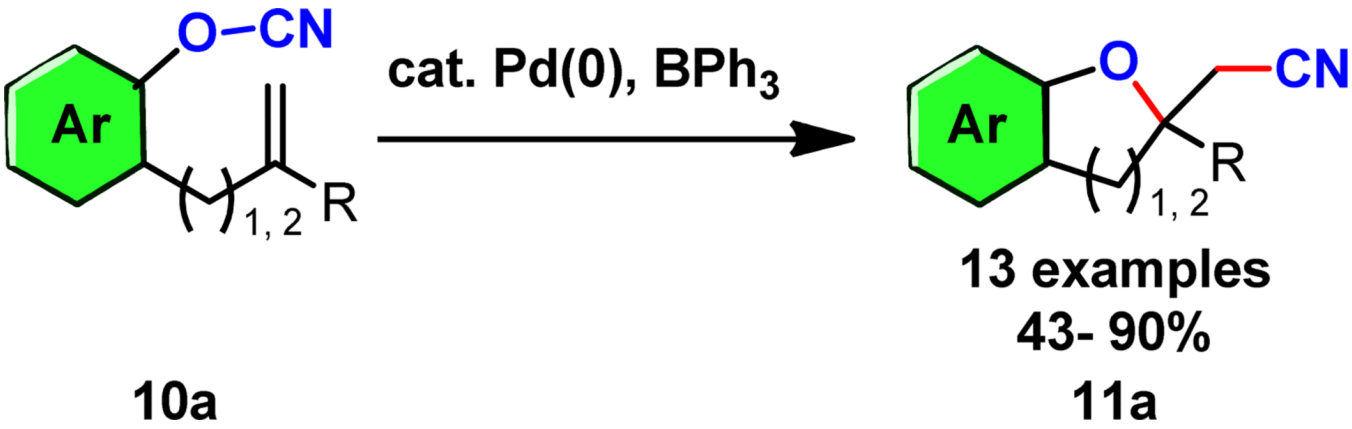
Scheme 2.
Scope of rhodium catalyzed C-CN bond transformation.



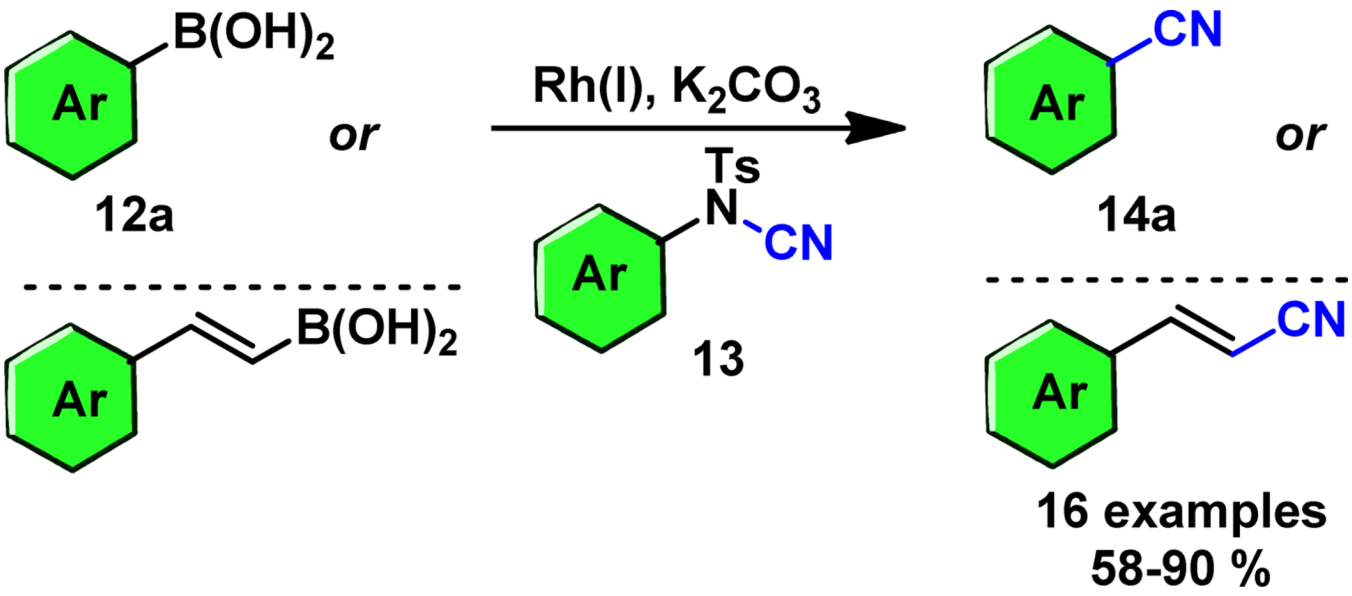
Scheme 3.
Pathways of metal catalyzed oxidative addition to R-CN.



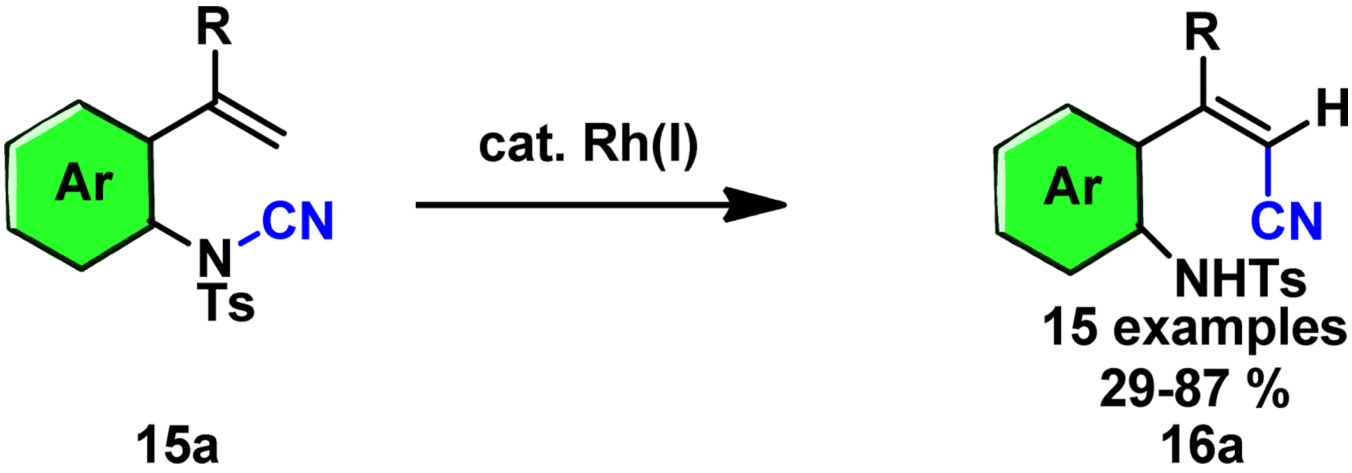
Scheme 4.
A possible mechanistic pathway.



Scheme 5.
Pd(0) catalyzed BPh_3 mediated O-CN bond activation.

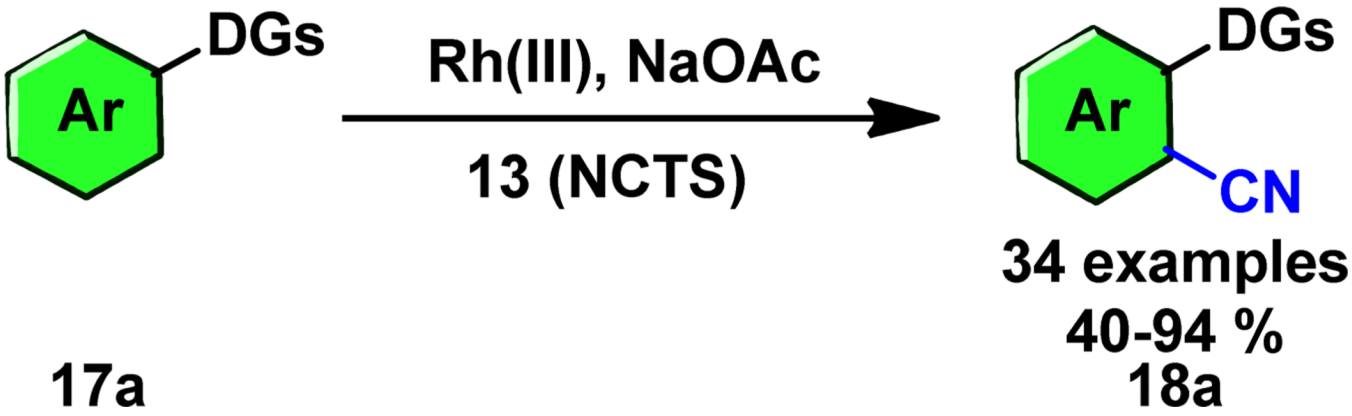


Scheme 6.
Aryl or styrenyl cyanate formation via N-CN cleavage.



15a 16a

Scheme 7.
Intramolecular cyanation via N-CN bond activation.



Scheme 8.
Aryl cyanation using intermolecular N-CN activation.

Table 1

Bonds dissociation energies of selective bonds.

Bond	Bond Dissociation Energies (KJ/mol)
H-C [a]	413
C-C	607
N-C	305
O-C	360
O-CN [b]	ca.358–799
N-CN [c]	ca.497
C-CN [c]	ca 555

***Notes*:**

[a] C_{sp2} in arene group;

[b] estimated value between C-O and C=O bonds, see reference 6a

[c] essential information see: Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC, Press, Boca Raton, FL, **2007**.