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Reductive coupling of nitro compounds with boronic acid derivatives: an overview

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The purpose of this review is to summarize the current literature on reductive C–N coupling of nitro compounds and boronic acids, with special emphasis on the mechanistic features of the reactions. The metal-catalyzed reactions are discussed first. This is followed by electro-synthesis and organophosphorus-catalyzed reactions. Finally, the available examples of catalyst-free reactions will be covered at the end of this review.

1. Introduction

Secondary (hetero)arylamines are common structural motifs encountered in the architecture of numerous natural products,¹ pharmaceutical agents,² and agrochemicals (Scheme 1).³ Due to their wide importance in diverse fields, over the years, a number of synthetic approaches have been developed for their preparation. The most general transformations include direct alkylation of (hetero)aromatic amines with alkyl halides,⁴ Buchwald–Hartwig,⁵ Ullmann,⁶ and Chan–Lam–Evans⁷ and cross-coupling reactions. Without exception, all these strategies utilize free amines as the nitrogen source. As it is well-known, the main method for the preparation of primary amines, especially for anilines, is stoichiometric reduction of the corresponding nitro compounds.⁸ Indeed, a recent study on the most-used reactions in medicinal chemistry found reduction of nitroarenes to anilines was the most-used reduction.⁹ Therefore, without question, the development of efficient and practical approaches for the synthesis of titled compounds directly from the corresponding nitro compounds is extremely desirable in terms of saving energy and time.¹⁰

In this context, recently, reductive C–N coupling of abundant and readily available nitro compounds with stable and non-toxic boronic acid derivatives has attracted more and more attention as a general and straightforward route for the construction of secondary amines (Fig. 1), which beside high step economy, using non-toxic and easily accessible starting materials, high functional group tolerance, simplicity as well as avoiding the pre-preparation of amine substrates can be considered as the main advantages of this synthetic strategy over conventional methodologies.

Despite the significant progress that has been achieved in this attractive research topic over the past five years, a comprehensive review has not appeared on this hot and fast-growing arena in the literature thus far. As a continuation of our previous works on modern cross-coupling reaction,¹¹ herein, we will try to provide an updated overview of the most important advances and developments of the reductive C–N coupling of nitro compounds with boronic acids with special emphasis on the mechanistic features of the reactions. For clarity, the review was structured based on the type catalysts (*i.e.*, metal-catalyzed, electro-catalyzed, organophosphorus-catalyzed, catalyst-free reactions).

2. Metal-catalyzed reactions

Reductive C–N coupling of nitro compounds and boronic acid derivatives with the assistance of a metal-catalyst is probably the area that has experienced the most growth in the field in the last few years. In 2019, Pantiga, Sanz, and co-workers demonstrated for the first time the usefulness of metal catalysts for reductive amination of boronic acids with nitro compounds.¹² Thus, in the presence of 5 mol% of MoO₂Cl₂(dmf)₂, as a catalyst and 2,2'-bipyridine (bpy) as a ligand, in combination with 2.4 equiv. of PPh₃ as a reducing agent in toluene at 100 °C, the reaction of nitro(hetero)arenes **1** with various (hetero)aryl and alkyl boronic

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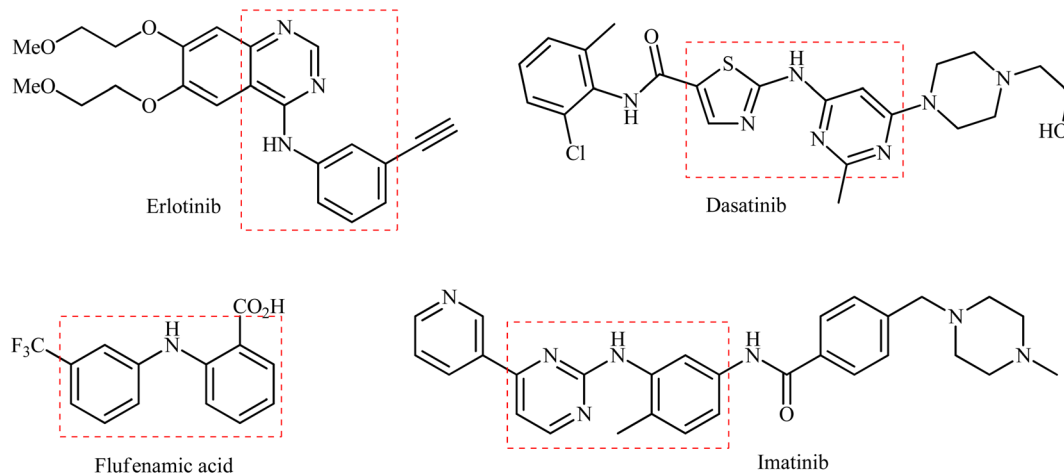
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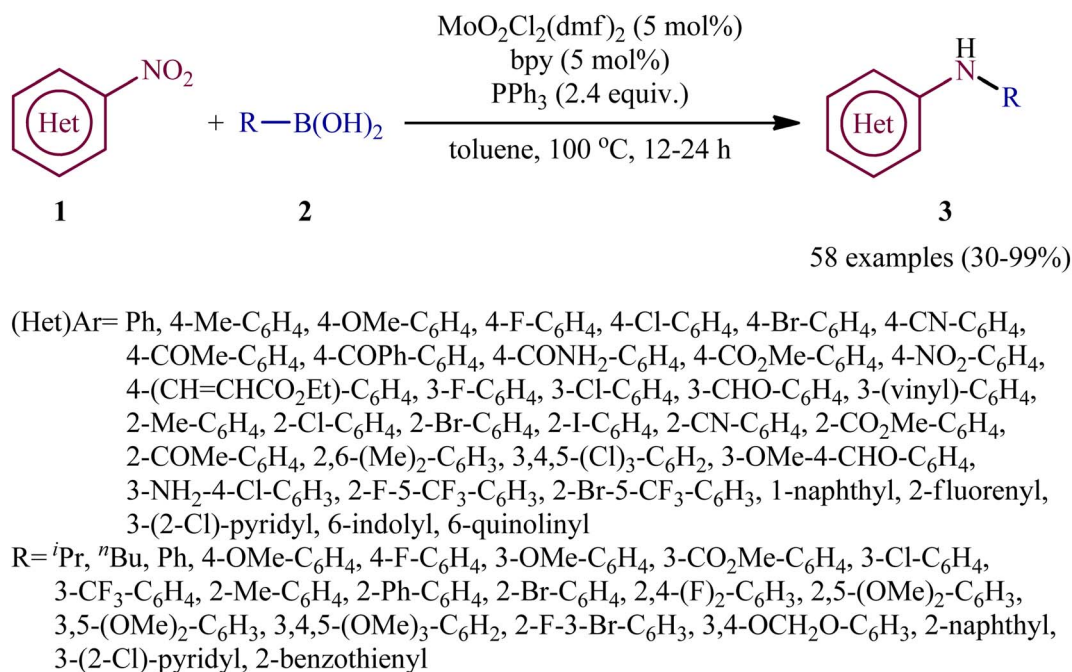



Scheme 1 Selected examples of pharmaceutically important (hetero)arylamine derivatives.



Fig. 1 Direct reductive coupling of nitro compounds with boronic acids.

acids **2** furnished the corresponding secondary amines **3** in moderate to quantitative yields, ranging from 30% to 99% (Scheme 2). The reaction tolerated a wide panel of important functional groups (*e.g.*, F, Cl, Br, I, CF₃, CN, NH₂, COMe, CO₂Me, CONH₂, CHO), which might provide potential opportunities for further manipulation of amine products. Particularly remarkable is that the reaction exhibited extremely high degree of site-selectivity, in which amination is exclusively took place over the nitro group when free amine is also present without the need for protecting group chemistry. It is worthwhile to note that reductive arylation of aliphatic nitro compounds including nitromethane, nitroethane, 2-nitropropane, 1-nitrohexane, and ethyl 2-nitroacetate was also

Scheme 2 Mo-catalyzed reductive C–N coupling of nitro(hetero)arenes **1** with boronic acids **2**.

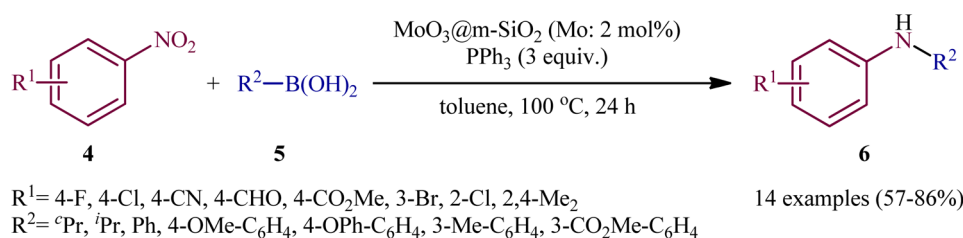


Scheme 3 Mechanism that accounts for the formation of secondary amines 3.

achieved with use of similar reaction conditions. However, they were slightly sluggish to participate in this protocol and required microwave (MW) irradiation to achieve full conversion (7 examples, 51–72%). Unfortunately, no comment was made by the authors regarding the relationship between structure of starting materials and their associated catalytic activity as well as regarding the recovery and reusability of the catalyst. According to the authors proposed mechanism (Scheme 3), this C–N coupling reaction might start with the generation of Mo species B via the reduction of dioxomolybdenum(vi) catalyst A with PPh₃ to a Mo^{IV} species followed by coordination to the nitro compound 1. Subsequently, reoxidation of the Mo center by the coordinated nitro compound gives intermediate C bearing a nitroso ligand, which after the second deoxygenation with PPh₃ and subsequent reduction of the nitroso ligand and reoxidation of the metal center converts to molybdooxaziridine (or η²-nitroso) species D (Scheme 3, path A). Next, the attack of the N atom of species D to the boronic acid 2 leading to the formation of nitrenoid intermediate E, which undergoes

a rearrangement to yield aminoboronic acid F. In another possibility (Scheme 3, path b), intermediate C releases a free nitroso compound G and regenerates catalyst A. Subsequently, the former reacts with another molecule of PPh₃ to afford the reduced adduct H, which after interaction with the boronic acid 2 delivers nitrenoid borate intermediate I. Later, 1,2-migration of a nucleophilic R² group to adjacent N center and spontaneous release of O=PPh₃ leads to the formation the same aminoboronic acid F. Finally, hydrolysis of this intermediate F affords the observed amine 3.

Two years later, Song and colleagues developed this chemistry using a novel heterogeneous catalyst composed of nanoporous MoO₃ confined in mesoporous silica (MoO₃@m-SiO₂).¹³ Thus, with the assistance of only 2 mol% MoO₃@m-SiO₂ (based on Mo atoms) and 3 equivalent PPh₃, a variety of nitroarenes 4 reacted with aryl/alkyl boronic acids 5 under an inert atmosphere to afford the target N-arylamine products 6 in good to high yields within 24 h (Scheme 4). Noteworthy, recycling tests indicated that the catalyst could be reused at least for five



Scheme 4 Reductive coupling of nitroarenes 4 with aryl/alkyl boronic acids 5 catalyzed by MoO₃@m-SiO₂.





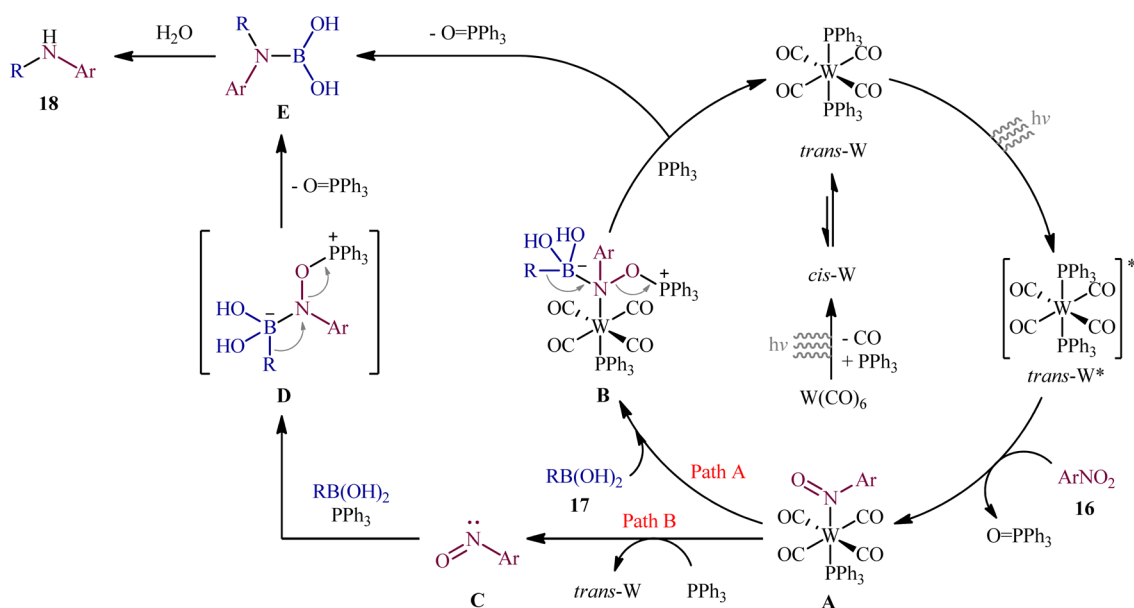
(Het)Ar= Ph, 4-Me-C₆H₄, 4-Et-C₆H₄, 4-F-C₆H₄, 4-Cl-C₆H₄, 4-CN-C₆H₄, 4-CF₃-C₆H₄, 4-CHO-C₆H₄, 4-CO₂Me-C₆H₄, 4-COMe-C₆H₄, 4-O-allyl-C₆H₄, 3-F-C₆H₄, 3-Br-C₆H₄, 3-CF₃-C₆H₄, 2-Cl-C₆H₄, 3,5-(CF₃)₂-C₆H₃, 3-OMe-4-Me-C₆H₃, 2-OMe-4-F-C₆H₃, 2-Cl-4-Me-C₆H₄, 3-(6-OMe)-pyridyl, 5-(1-Me)-indolyl, 1-fluorenyl, 6-isobenzofuran-1(3*H*)-one-yl

R= ⁱPr, ^cPr, ⁿBu, ^cPent, ^cHex, CH₂Bn, Ph, 4-Et-C₆H₄, 4-ⁿPr-C₆H₄, 4-OMe-C₆H₄, 4-OPh-C₆H₄, 4-SMe-C₆H₄, 4-F-C₆H₄, 4-Cl-C₆H₄, 4-Br-C₆H₄, 4-COPh-C₆H₄, 3-Me-C₆H₄, 3-Ph-C₆H₄, 3-CO₂Me-C₆H₄, 5-indolyl, 3-(6-F)-pyridyl

Scheme 9 Visible-light induced, tungsten-catalyzed amination of boronic acids **17** with nitro(hetero)arenes **16**.

reductive arylation of nitroarenes with aryl boronic acids.¹⁸ The electrolysis was performed with a platinum plate anode and a carbon cloth cathode in an undivided cell, with hexafluoroisopropanol (HFIP)/MeCN/HCO₂H as the mixed solvent containing ⁿBu₄NBr as the supporting electrolyte and triethyl phosphite [P(OEt)₃] as a reducing agent under a constant current of 10 mA (Scheme 11). The transformation was suitable for several nitroarenes **19** and a variety of electron rich- and deficient-substituted aryl boronic acids **20** and the desired diarylamines **21** were obtained in fair to good yields. However, when methoxy- or trifluoromethyl-substituted nitroarenes were employed under the optimal reaction conditions, only corresponding amino compounds were obtained. Furthermore, the process is not viable for gram-scale due to the drastic reduction in the yield (from 75% in the 0.2 mmol scale, to 60% in the 5.0 mmol scale). The main features of this method are the mild

reaction conditions and carried out in a short reaction time. It is interesting to mention that under the standard reaction conditions, replacing nitroarenes by either anilines or 1,2-diazydiazenes stopped the reaction completely. Since this electro-synthesis was doable with or without presence of a reducing agent, although the best results were observed in the presence of P(OEt)₃, two possible mechanisms were proposed by the authors for this transformation (Scheme 12). In pathway A, nitroarene **19** is reduced to the nitroso compound **A** by two-electron uptake from the cathode and losing a water molecule with the help of acid. Next, with the coordination of the nitroso intermediate **A** with arylboronic acid **20** and receiving one electron from the cathode, intermediate **C** is generated. This intermediate is then converted to diarylboramidic acid **D** via aryl migration and another dehydration process. Finally, through the protonation of intermediate **D**, the expected



Scheme 10 Mechanistic proposal for the reaction in Scheme 9.



Scheme 11 Yi–Lei's synthesis of diarylamines **21**.

Scheme 12 Plausible mechanism for the reaction in Scheme 11.

diarylamine **21** is formed. On the other hand, in pathway B through the nucleophilic attack of a lone-pair electron of P(OEt)_3 on the oxygen atom of the nitro group of nitroarene **19**, followed by the acceptance of one electron from the cathode, the reactive species **E** is generated, which after receiving one electron from the cathode and losing a EtOH and HOP(OEt)_2 with the help of acid, transformed to the nitroso compound **A**. It has been suggested that both pathways may be operative at the same time. To the best of our knowledge, this is the first and only example reported on the electrochemical reductive arylation of nitroarenes with arylboronic acids till date.

4. Organophosphorus-catalyzed reactions

In recent years, organophosphorus compounds have been extensively used as catalysts in a variety of synthetic reactions and in drug development.¹⁹ Particularly, chiral organophosphorus catalysts play an extremely important role in the field of asymmetric catalysis.²⁰ The first report on the utilization of phosphorus-based organocatalysis in the deoxygenative C–N cross-coupling between nitro compounds with boronic acid derivatives was published by Luzung and Radosevich along with their co-workers in 2018,²¹ who showed that the treatment of functionalized (hetero)aromatic nitro compounds **22** with various alkyl, aryl, as well as heteroaryl boronic acids **23** in the presence of a catalytic amount of 1,2,2,3,4,4-

hexamethylphosphetane ($\text{I} \cdot [\text{O}]$), a small-ring phosphacycle, and over-stoichiometric amounts of PhSiH_3 as a reducing agent in *m*-xylene, resulted in the formation of the corresponding secondary aryl amines **24** in moderate to excellent (Scheme 13). Remarkably, it was found that the reaction is stereospecific with respect to $\text{Csp}^3\text{-N}$ bond formation, when using the stereochemical probe molecules as substrate. The authors, also nicely exemplified the complementarity of their methodology for C–N coupling with respect to existing transition metal strategies (*i.e.*, Buchwald–Hartwig and Chan–Lam couplings) utilizing *N*-(3-bromo-5-nitrophenyl)acetamide as the reactant. The results indicated that whereas C–N coupling under Cu-mediated or Pd-catalyzed methods permitted chemoselective functionalization at the anilide or aryl bromide positions, respectively, catalytic arylation by the newly developed organophosphorus-catalyzed coupling approach resulted in selective functionalization at the nitro moiety. Unfortunately, the applicability of aliphatic nitro compounds as starting materials was not investigated in this study.

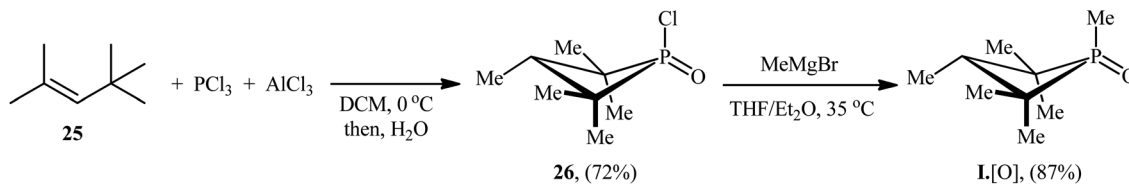
The synthetic route for the preparation of $\text{I} \cdot [\text{O}]$ is shown in Scheme 14.²² The key step in this synthesis was to prepare the intermediate phosphetane oxide **26** *via* treatment of 2,4,4-trimethyl-2-pentene **25** with phosphorus trichloride (PCl_3) in the presence of aluminum chloride.

In a subsequent extension of the substrate scope of the methodology, it was shown that various functionalized aryl boronic acids **27** could be treated with 3 equiv. of nitromethane





Scheme 13 Luzung–Radosevich's synthesis of secondary aryl amines 24.



Scheme 14 Synthesis of I.[O] developed by Radosevich.

(MeNO₂) under the same catalytic system in refluxing cyclopentyl methyl ether (CPME) to give the corresponding *N*-methylanilines 28 in moderate to excellent yields (Scheme 15).²³ The system was also amenable to the methylation reaction of aryl boronic acids with the nitromethane isotopologue (*viz.* ²H₃C–NO₂, ¹³H₃C–NO₂, ¹⁵H₃C–NO₂), providing isotopically labeled *N*-methylaniline products in high yields. It should be mentioned that apart from aryl boronic acids, aryl boronic esters were also compatible with this methylation scenario. In order to further value the applicability of the method, the authors elegantly synthesized triflubazam (an anxiolytic drug) from commercially available 4,4,5,5-tetramethyl-2-(2-nitro-5-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane through a two-pot, three step procedure

involving two P^{III}/P^V-catalyzed deoxygenative C–N cross-coupling steps.

Subsequently, based on the above catalyst, this research group developed an improved catalytic system by replacing PhSiH₃ with PMHS and performing the process in CPME, which resulted in a broader substrate scope and significantly improved yields.²⁴ Thus, with the modified “second-generation” conditions, a library of heteroaryl nitro substrates 27 engaged effortlessly with various heteroaryl boronic acids 30 to give the corresponding di(hetero)arylamines 31 in good yields (Scheme 16). In this report, several control experiments, such as DFT calculation and spectroscopic studies, were conducted for the insight of the reaction mechanism, which indicated a two-stage deoxygenation sequence for this reductive C–N coupling

Scheme 15 P^{III}/P^V-catalyzed methylation of arylboronic acids 27 with MeNO₂.



(Het)Ar¹ = 4-CF₃-C₆H₄, 3-pyridyl, 6-quinolynyl, 5-isoquinolynyl, 5-(1-Me)-indolyl, 4-(1-Me)-pyrazolyl, 5-(2,3-Me₂)-indazolyl, 6-(2-NHCOMe)-benzothienyl, 5-[2-(4-Et-piperazin-1-yl)]-pyrimidyl
 (Het)Ar² = Ph, 4-F-C₆H₄, 2-Me-3-Cl-C₆H₃, 3-(2-OMe)-pyridyl, 4-(1-Bn)-pyrazolyl, 5-(1-Me)-indazolyl, 5-(2,4-OMe₂)-pyrimidyl

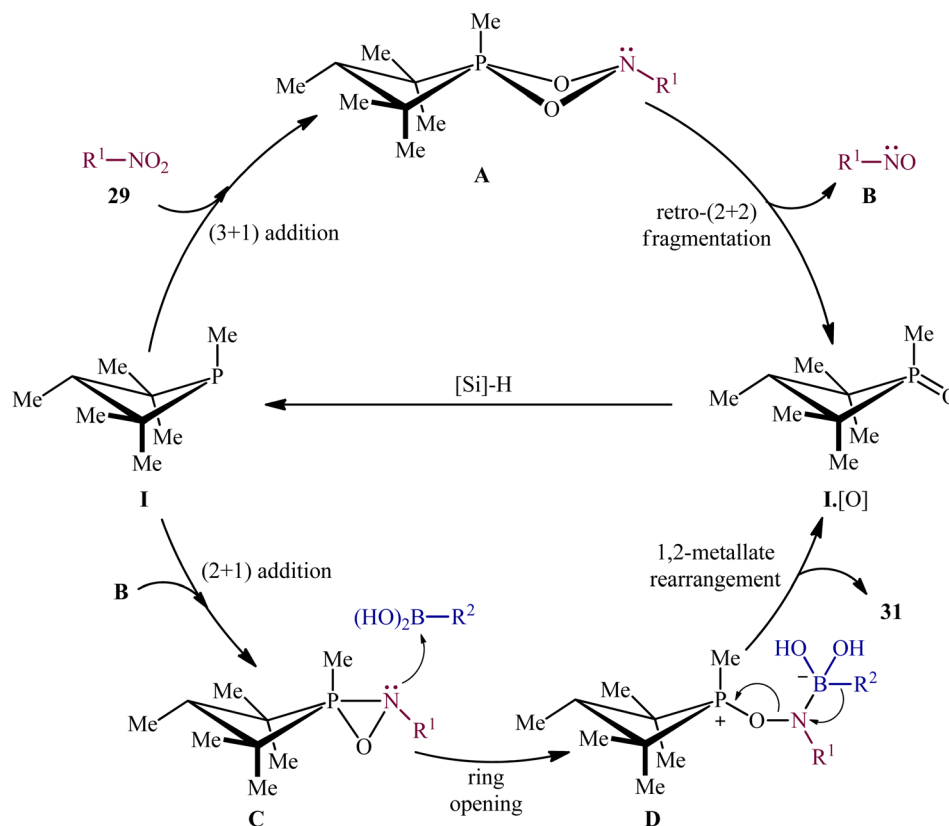
Scheme 16 P(III)/P(V)-catalyzed reductive C–N coupling of nitro(hetero)arenes **29** and (hetero)aryl boronic acids **30** using PMHS as the reductant.

(Scheme 17).^{24,25} The first cycle starts with the [3 + 1] cheletropic addition of nitro compound **29** to phosphetane **I** leading to the formation of cycloadduct **A**, which undergoes a retro-[2 + 2] fragmentation to furnish the corresponding nitroso compound **B** and phosphetane oxide **I**·[O]. Finally, the later rapidly converts to **I** through reduction by the hydrosilane. In the second cycle, a [2 + 1] addition between the nitroso compound **B** and phosphetane **I** affords oxazaphosphirane **C**, which then reacts with boronic acid **30** to furnish betaine intermediate **D**. Finally, 1,2-metallate rearrangement of intermediate **D** yields the expected product **31**.

Later, this innovative research group undertook in-depth experimental kinetics and computational studies to elucidate

the barriers to the compatibility of their methodology with nitroalkanes as coupling partners.²⁶ The results indicated that a steric perturbation on the phosphorus catalyst **I**·[O] is a key factor that disrupts the desired reaction pathway when nitroalkanes were used as the substrates (Fig. 2). Therefore, a small peripheral alteration to the catalyst dramatically improves the efficiency of reductive coupling of nitroalkanes with boronic acids.

Very recently, this creative research team disclosed that treatment of readily available 2-nitropropane with various (hetero)aryl boronic acids in the presence of a catalytic amount of sterically reduced phosphetane **II**·[O] resulted in good yields of corresponding primary anilines through the Nef decomposition



Scheme 17 Mechanistic proposal for the P(III)/P(V)-catalyzed reductive C–N coupling of nitro compounds **29** and boronic acids **30**.





Fig. 2 Steric considerations enable P(III)/P(V)-catalyzed reductive C–N coupling of nitroalkanes and boronic acids.



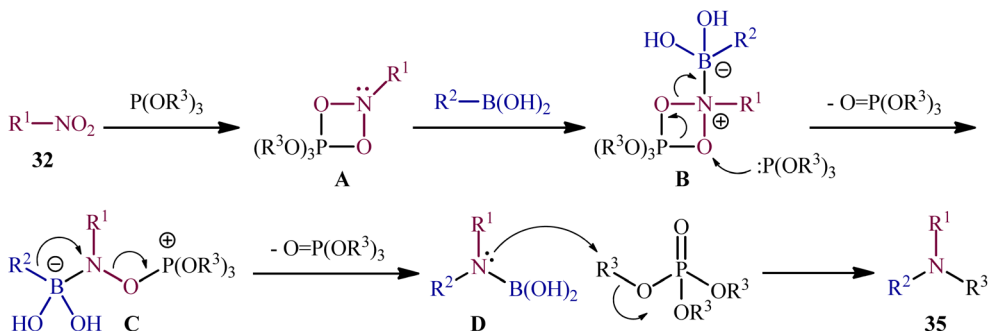
Scheme 18 Catalyst-free three-component coupling of nitro compounds **32**, boronic acids **33**, and trialkyl phosphites **34**.

of 2-nitropropane to form the nitroxyl intermediate HNO followed by **II**·[O]-catalyzed reaction with boronic acids.²⁷

5. Catalyst-free reactions

As a continuation of their previous work on the synthesis of di(hetero)arylamines through the transition-metal-free cross-coupling between nitrosoarenes and boronic acids in the presence of a trivalent phosphorus species,²⁸ in 2020, Roscales and Csáky reported a beautiful protocol for the synthesis of tertiary aromatic amines **35** through the three-component reaction between nitro compounds **32**, boronic acids **33** and trialkyl phosphites **34** under catalyst- and additive-free conditions (Scheme 18).²⁹ Interestingly, in this reaction trialkyl phosphites

played multiple roles; the substrate, solvent, and mediator. The transformation was very general and functional-group tolerant, compatible with a wide variety of nitro compounds, including aromatic (electron-rich and -poor), aliphatic (primary and secondary), and benzylic nitro compounds. In additions, the scope of boronic acids that underwent reaction was broad enough to include alkyl, aryl, and heteroaryl boronic acid derivatives. Additionally, various functionalized phosphites (primary and secondary, including halogen functionalization) were well tolerated by this method. The broad synthetic applicability of this three-component reaction was further demonstrated by performing reductive engaging of the corresponding α -nitro esters with aryl boronic acids and trialkyl phosphites to give biologically important α -amino esters. According to the



Scheme 19 Possible mechanism for the formation of tertiary aromatic amines **35**.





Scheme 20 PPh₃-mediated reductive coupling of nitro(hetero)arenes **36** and boronic acids **37** reported by Radosevich.

authors, this reaction most likely proceeds through an azadioxaphosphetane intermediate **A**, as depicted in Scheme 19.

In a related investigation, Radosevich's research team reported the synthesis of a library of (hetero)arylamines **38** *via* reductive C–N coupling of corresponding nitro(hetero)arenes **36** and boronic acids **37** using PPh₃ as a mediator without addition of any transition metal catalysts/additives.³⁰ The reactions carried out in *m*-xylene at 120 °C, tolerated a series of sensitive functional groups (*e.g.*, OMe, F, Cl, Br, I, Bpin, NH₂), and provided the desired amine products in moderate to good yields, within hours (Scheme 20). The protocol was compatible with both aromatic and aliphatic boronic acids and various nitro(hetero)arenes. The results demonstrated that the nitroarenes bearing electron-withdrawing afforded better yields compared to electron-donating groups ones. On the other hand, aromatic boronic acids gave higher yield of coupling products than aliphatic and benzylic acids.

With the aim of designing a milder procedure to aryl amines through catalyst-free deoxygenative C–N coupling of nitroarenes and boronic acids, Baitalik and Jana along with their colleagues were able to demonstrate that a diverse range of *N*-substituted

aniline derivatives **41** (52 examples) could be obtained in fair to good yields (up to 86%) from the reaction of corresponding nitro(hetero)arenes **39** with boronic acids **40** (aliphatic, aromatic and heteroaromatic) in the presence of 2 equiv. PPh₃ under the irradiation of visible light at 30 °C, in the absence of any photoredox catalyst (Scheme 21).³¹ However, the process is not viable for gram-scale due to the noticeable reduction in the yield (from 86% in the 0.2 mmol scale, to 70% in the 4.0 mmol scale). Based on literature and the experimental results, the authors suggested a plausible mechanism for this C–N bond forming reaction as depicted in Scheme 22. The transformation may start with the singlet excited state of nitroarene *via* the excitation of nitroarene **39** under visible light irradiation, which after ultrafast intersystem crossing and electron transfer from PPh₃ affords the nitroso compound **B** through the redox couple **A**. Subsequently, that nucleophilic addition of another molecule of PPh₃ to the oxygen of the nitroso compound **B** leads to the formation of tetravalent phosphorus intermediate **C**, which after decomposition affords the nitrene intermediate **D** and 1 equiv. O=PPh₃. Thereafter, the newly formed intermediate **D** undergoes nucleophilic addition to the boronic acid **40** to form



Scheme 21 Visible-light- and PPh₃-mediated reductive coupling of nitro(hetero)arenes **39** with boronic acids **40**.





Scheme 22 The plausible mechanism for the reactions in Scheme 21.

the boronate species **E**, which then undergoes a rearrangement to give the aminoboronic acid **F**. Finally, hydrolysis of this intermediate **F** affords the desired amine **41**.

Another independent light-mediated reductive amination method was published by Song–Yang and co-workers³² almost using identical conditions demonstrated by Baitalik and Jana group.³³ However, in this method, the reaction was performed in toluene using an UV lamp (365 nm) as the light source. Although various nitro(hetero)arenes, and aromatic boronic acids were well tolerated under the reaction conditions, aliphatic boronic acids did not respond the reaction under standard conditions.

6. Conclusion

The direct reductive coupling of widely available nitro compounds with boronic acids has recently emerged as the reliable, powerful, and step-economical approach for the construction of biologically and synthetically important secondary amines in a one-pot manner, without the need to isolation of intermediates and use of pre-prepared amine substrates. As illustrated, this novel strategy for C–N bond formation was successfully applied for the construction of various C(sp²)-N-C(sp²) and C(sp³)-N-C(sp²) bonds. However, its applicability in the formation of C(sp³)-N-C(sp³) bonds was not investigated. Therefore, many more studies are needed to extend this chemistry to C(sp³)-N-C(sp³) bond formation. In addition, the majority of reactions covered in this review were performed at elevated temperatures. Thus, further research is still needed to development of efficient catalytic systems that allow this C–N bond forming reaction under milder conditions. Additionally, the scope of nitro compounds is largely limited to nitroarenes. Therefore, methodologies compatible with nitroalkanes should be developed.

Conflicts of interest

There are no conflicts to declare.

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