

Review

Metal-Free One-Pot Multi-Functionalization of Unsaturated Compounds with Interelement Compounds by Radical Process

Yuki Yamamoto  and Akiya Ogawa *

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Osaka 599-8531, Japan

* Correspondence: ogawa@omu.ac.jp

Abstract: In recent years, the importance of “environmentally friendly manufacturing” has been increasing toward the establishment of a resource-recycling society. In organic synthesis, as well, it is becoming increasingly important to develop new synthetic strategies with resource conservation and the recycling of elemental resources in mind, rather than just only synthesis. Many studies on the construction of frameworks of functional molecules using ionic reactions and transition-metal-catalyzed reactions have been reported, but most of them have focused on the formation of carbon–carbon bonds. However, it is essential to introduce appropriate functional groups at appropriate positions in molecules in order for the molecules to express their functions, and furthermore, the highly selective preparation of multiple functional groups is considered important for the creation of new functional molecules. In this review, we focus on radical reactions with high functional group selectivity and overview the recent progress in practical methods for the simultaneous introduction of multiple functional groups and propose future synthetic strategies that emphasize the recycling of elemental resources and environmental friendliness.

Keywords: heteroatoms; interelement compounds; metal-free conditions; radical reaction; unsaturated compounds; functionalization



Citation: Yamamoto, Y.; Ogawa, A. Metal-Free One-Pot Multi-Functionalization of Unsaturated Compounds with Interelement Compounds by Radical Process. *Molecules* **2023**, *28*, 787. <https://doi.org/10.3390/molecules28020787>

Academic Editors: Vadim A. Soloshonok and Roman Dembinski

Received: 30 November 2022

Revised: 8 January 2023

Accepted: 9 January 2023

Published: 12 January 2023



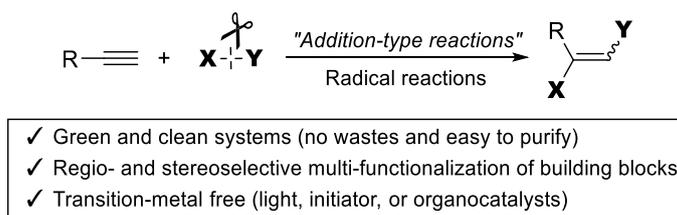
Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In recent years, “environmentally friendly manufacturing” has become increasingly important to construct a resource-recycling society. In particular, many efforts have been made to reduce wastes in the synthesis of functional molecules in the field of pharmaceuticals, biotechnology, and functional material chemistry, but there remain many challenges to be overcome. Many studies on the construction of the scaffolds of functional molecules using ionic reactions and transition-metal-catalyzed reactions have been reported, but most of them have focused on carbon–carbon bond formation [1–5]. However, in order for a molecule to express a special function, it is essential to introduce an appropriate functional group at an appropriate position in the molecule. For the creation of more innovative functional molecules, molecules with multiple carbon–heteroatom bonds are expected to be important candidates that can impart various functions. From this perspective, attention is focused on the development of innovative synthetic methods that simultaneously introduce multiple functional groups while ensuring the resource conservation of elemental resources [6–9].

The introduction of different heteroatoms into building blocks has been studied primarily on the basis of ionic reactions. The “substitution reaction”, which is often seen in ionic reactions, generates large amounts of wastes as byproducts. Recently, methods using transition metal catalysts have also been reported, but these methods involve significant costs for waste disposal and the removal of metal residue in the products. Therefore, the development of more practical and atom-efficient methods is desired [10–12].

Hence, this review focuses on metal-free reactions, especially radical reactions with excellent functional group selectivity. Among the radical reactions, “radical addition reactions” can incorporate all starting substrates into the product and can be regarded as a more atomically efficient synthetic method compared to substitution-type reactions involving the byproduction of leaving groups. Since each heteroatom has individual properties in radical reactions, highly selective multi-functionalization is possible by appropriately combining heteroatom reagents [13,14]. Interelement compounds, which have heteroatom–heteroatom linkages, are expected to be very effective for the simultaneous introduction of multiple heteroatom functional groups, because heteroatom-centered radicals can be generated by homolysis under photoirradiation [15,16]. Thus, molecular design using interelement compounds is highly expected to become an important fundamental technology for organic synthesis in the future (Scheme 1).

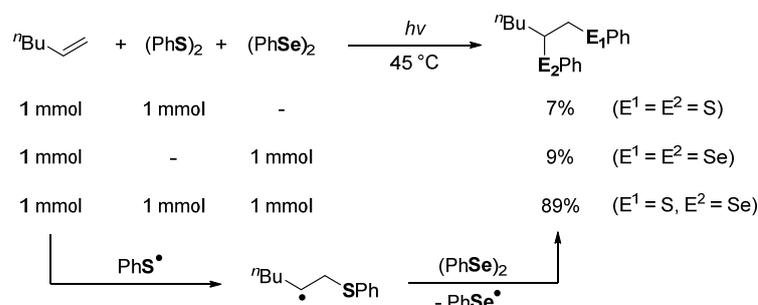


Scheme 1. General concept for the utilization of heteroatom-centered interelement compounds in the radical multi-functionalization of building blocks.

In this review, we present recent progress in the environmentally harmonized synthesis of carbon–heteroatom bonds by radical addition reactions to unsaturated compounds using group 13, 15, and 16 interelement compounds. Owing to their relatively strong dissociation energies, bond cleavage in the radical reactions of group 14 interelement compounds is disadvantageous. Instead, transition-metal-catalyzed addition reactions have been used effectively [17–20]. In the case of interelement compounds containing halogen, addition reactions usually proceeded by ionic pathways in preference to radical pathways. Therefore, group 14 and 17 interelement compounds are not dealt with here. This review also deals with future perspectives for radical reactions of interelement compounds.

2. The Group 16 Element (O, S, Se, and Te)-Centered Interelement Compounds in Radical Reactions

Previously, we developed a series of photoinduced addition reactions of organochalcogen interelement compounds to various unsaturated compounds [21–27]. During these studies, we noticed the combination of two kinds of interelement compounds is very important to induce efficient radical addition reactions. For example, diphenyl disulfide or diselenide alone could not add to alkenes efficiently; however, the use of them together successfully induced an efficient and regioselective thioselenation of alkenes (Scheme 2).

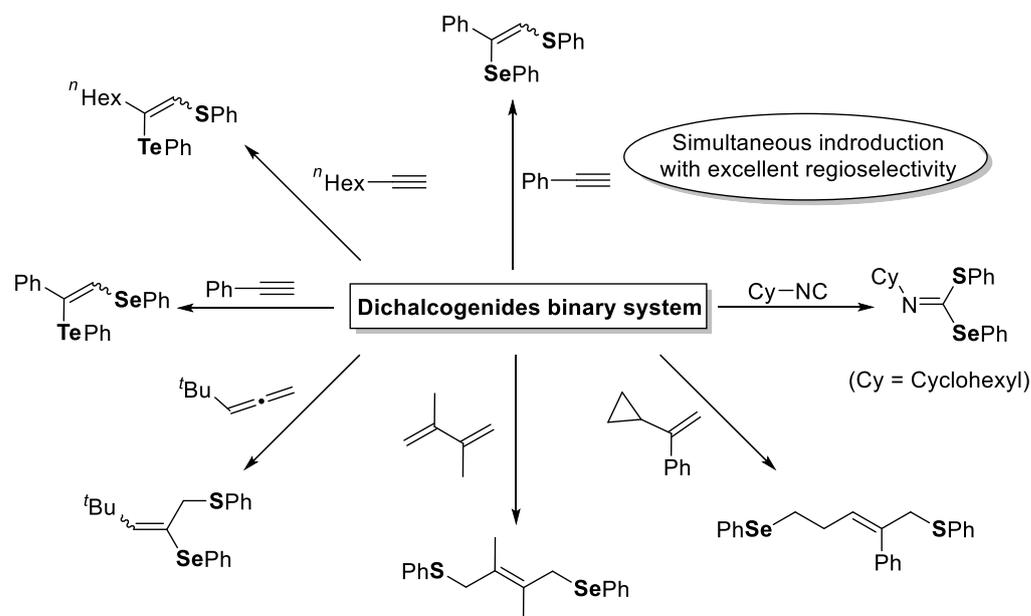


Scheme 2. Photoinduced thioselenation of alkenes using $(\text{PhS})_2/(\text{PhSe})_2$ -mixed system.

This is because of the relatively higher reactivity of $\text{PhS}\cdot$ ($k_{\text{PhS}\cdot}/k_{\text{PhSe}\cdot} = \text{ca. } 10\text{--}50$) and the relatively higher carbon-radical-trapping ability of $(\text{PhSe})_2$ ($k_{(\text{PhSe})_2}/k_{(\text{PhS})_2} = \text{ca. } 160$).

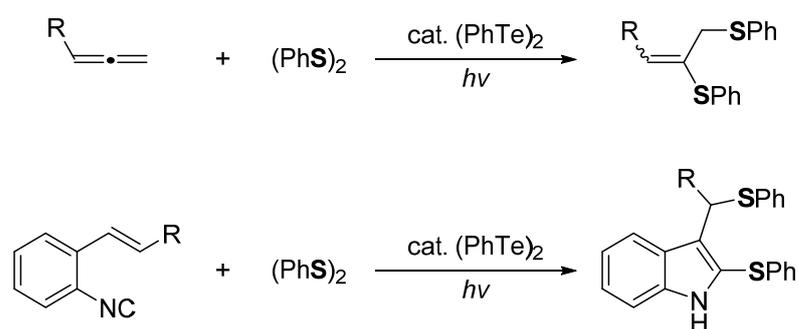
Therefore, PhS• selectively attacks the terminal position of alkenes, and the resulting β -phenylthio-substituted alkyl radicals are selectively captured by (PhSe)₂ [28].

As described here, the construction of mixed systems of organochalcogen interelement compounds effectively makes it possible to attain the simultaneous introduction of two chalcogen groups into unsaturated bonds with excellent regioselectivity. This concept can be applied to the radical addition reactions to a variety of unsaturated compounds, such as alkynes, allenes, conjugate dienes, vinylcyclopropanes, and isocyanides, as illustrated in Scheme 3 [29–33].



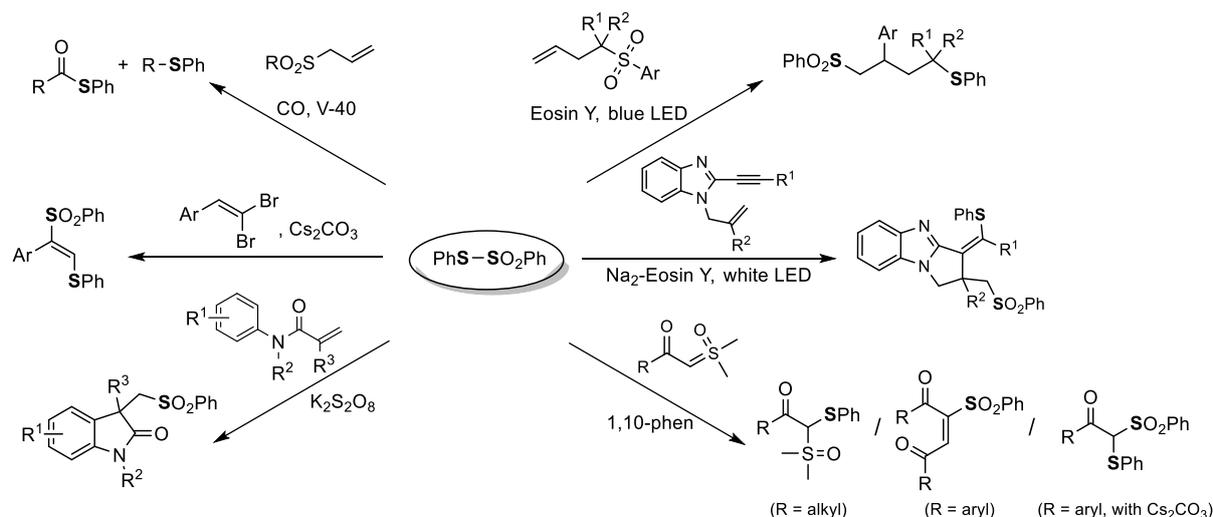
Scheme 3. Dichalcogenide binary systems for multi-functionalization of unsaturated compounds under light.

Furthermore, a mixed system of (PhS)₂ and (PhTe)₂ is also effective to introduce two chalcogeno groups into unsaturated bonds; especially, the catalytic use of (PhTe)₂ attained a novel dithiolation of allenes and *o*-ethenylaryl isocyanides (Scheme 4) [30,34].



Scheme 4. (PhTe)₂-catalyzed dithiolation of allenes and *o*-ethenylaryl isocyanides.

Thio- and selenosulfonate (PhS–SO₂Ph and PhSe–SO₂Ph) are reported to capture carbon radicals, and excellent examples using PhS–SO₂Ph for the introduction of sulfur-centered functional groups into several building blocks are shown in Scheme 5. In the presence of radical initiators or under light, the corresponding sulfur-centered radicals are generated from PhS–SO₂Ph, and sequential radical cascade reactions driven by trapping carbon radicals with them provide pharmaceutical and functional molecule scaffolds in one pot [35–40].



Scheme 5. Some examples of radical cascade reactions using thiosulfonates (PhS-SO₂Ph).

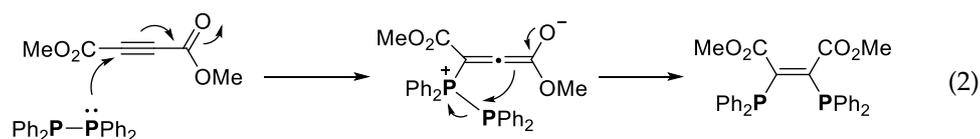
In sharp contrast, the combination of organic dichalcogenides ((RE)₂, E = S, Se, Te) and molecular halogen (X₂, X = Cl, Br, I) affords RE-X or RE-X₃, which are well-known to work as electrophilic reagents. Therefore, it is difficult to induce radical reactions in preference to ionic reactions. However, the binary system of Rf-I and (PhSe)₂ successfully attains the regioselective selenoperfluoroalkylation of alkynes by a radical pathway (Equation (1)) [41].



3. Phosphorus-Centered Interelement Compounds in Radical Reactions

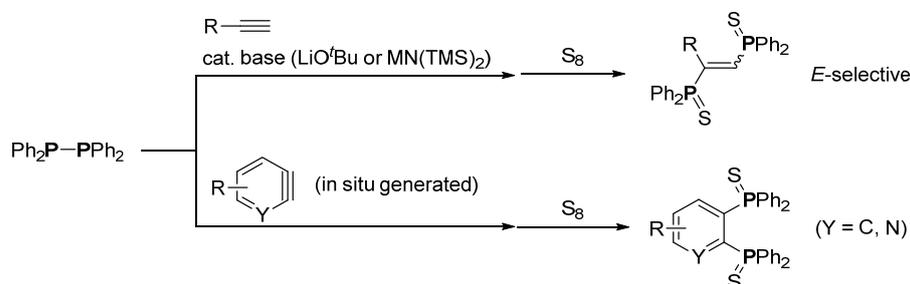
Among the interelement compounds bearing a P-P single bond, diphosphine (R₂P-PR₂), diphosphine monoxides (R₂P-P(O)R₂), diphosphine monosulfides (R₂P-P(S)R₂), and diphosphine disulfides (R₂P(S)-P(S)R₂) can be used for the simultaneous introduction of two phosphorus functional groups into unsaturated compounds [42,43]. In particular, diphosphines bearing P^{III}-P^{III} linkages have attracted many researchers to synthesize various bisphosphine ligands for organometallic chemistry and transition-metal-catalyzed reactions. For the highly efficient synthesis of phosphorus ligands, the simultaneous and stereoselective introduction of two phosphine units into unsaturated compounds is required, and effective methods by the addition of diphosphines have been developed over the past few decades [44].

Regarding the simultaneous introduction of two phosphine units by Ph₂P-PPh₂ via the ionic pathway, in 2006, Pringle et al. reported the stereospecific bisphosphination of activated acetylenes. In this reaction, a nucleophilic attack by Ph₂P-PPh₂ proceeds on an activated alkyne, such as dimethylacetylene dicarboxylate, and the subsequent intramolecular rearrangement of the generated zwitterionic intermediate gives the corresponding *vic*-diphosphinyl adduct as the exclusive *cis* isomer (Equation (2)) [45].



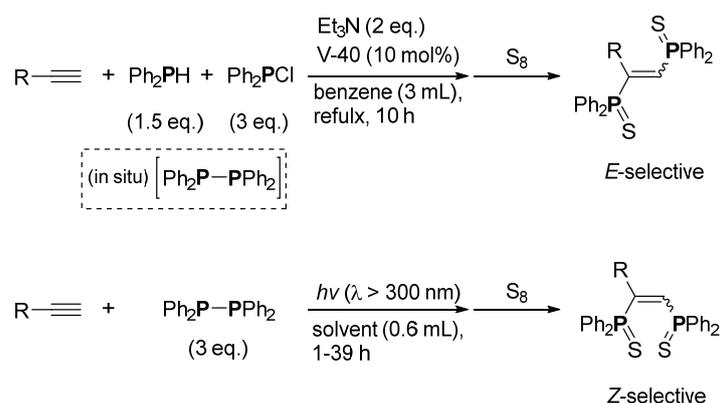
In 2017, Hirano and Miura et al. reported the stereoselective diphosphination of terminal alkynes by Ph₂P-PPh₂ in the presence of catalytic Brønsted bases [46]. In the case of terminal arylalkynes, the use of LiOtBu was found to be most effective, while the use

of $\text{MN}(\text{TMS})_2$ ($\text{M} = \text{Li}$ or Na) gave good results for aliphatic alkynes. This method gave the corresponding 1,2-diphosphinoethenes in good yields with excellent *E*-stereoselectivity. Moreover, they also developed the diphosphination of arynes, generated in situ from 2-(trimethylsilyl)aryl triflates and $\text{Bu}_4\text{NPh}_3\text{SiF}_2$ /or base, with $\text{Ph}_2\text{P}-\text{PPh}_2$ (Scheme 6) [47].



Scheme 6. Simultaneous introduction of two phosphine units into unsaturated compounds with $\text{Ph}_2\text{P}-\text{PPh}_2$ via ionic reactions.

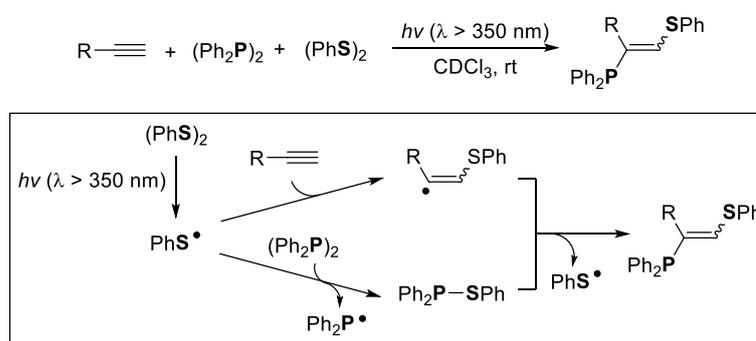
Diphosphines are also important as precursors of phosphorus-centered radicals [48,49]. Diphosphines and their analogues can undergo P-P single bond homolysis upon photoirradiation or radical initiators to generate the corresponding trivalent and/or pentavalent phosphorus-centered radicals, such as $\text{R}_2\text{P}^\bullet$ and/or $\text{R}_2\text{P}(\text{O})^\bullet$ [50–52]. An example of the radical addition of diphosphines to alkynes was reported by Yorimitsu and Oshima et al. in 2005 [53]. In this report, tetraphenyldiphosphine $\text{Ph}_2\text{P}-\text{PPh}_2$, generated in situ from diphenylphosphine and diphenylphosphine chloride in the presence of Et_3N , was allowed to react with alkynes under reflux for 10 h in the presence of a radical initiator, resulting in the corresponding *vic*-1,2-bisphosphinoalkenes with excellent *E*-stereoselectivity. Around the same time, we also developed the radical addition reaction of $\text{Ph}_2\text{P}-\text{PPh}_2$ to alkynes under light. In this photoirradiation system, the corresponding *vic*-1,2-bisphosphinoalkenes were obtained with *Z*-selectivity due to the photoinduced isomerization from *E*-adducts to *Z*-adducts (Scheme 7) [54].



Scheme 7. The radical addition of tetraphenyldiphosphine to alkynes.

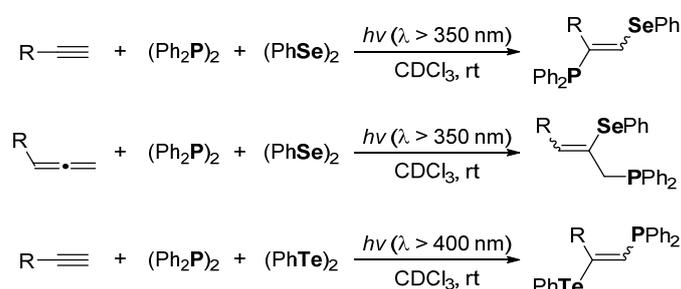
Furthermore, we also developed the photoinduced thiophosphination of alkynes by using the combination of $(\text{Ph}_2\text{P})_2$ and $(\text{PhS})_2$ in 2008 (Scheme 8) [55]. The absorption based on the $n-\sigma^*$ transition in the UV-visible spectrum of $(\text{PhS})_2$ reached 375 nm, confirming that irradiation with the light of wavelengths over 350 nm leads to the homolytic cleavage of the S-S bond to form PhS^\bullet . The generated PhS^\bullet reacted with alkynes and $(\text{Ph}_2\text{P})_2$ to form vinyl radical species and $\text{Ph}_2\text{P}-\text{SPh}$, respectively. Then, the generated vinylic radical was captured by $\text{Ph}_2\text{P}-\text{SPh}$ to afford the thiophosphinated products with excellent regio- and stereoselectivity. Yorimitsu and Oshima et al. reported in 2008 that the reaction of $\text{Ph}_2\text{P}-\text{SPh}$ with alkynes could also be conducted by using radical initiators [56]. In 2009, they also

developed the regio- and stereoselective synthesis of 1-aryl-1-thio-2-thiophosphinylene derivatives using $\text{Ph}_2\text{P}(\text{S})\text{-SR}$ analogues, with catalytic peroxide as the radical initiator [57].



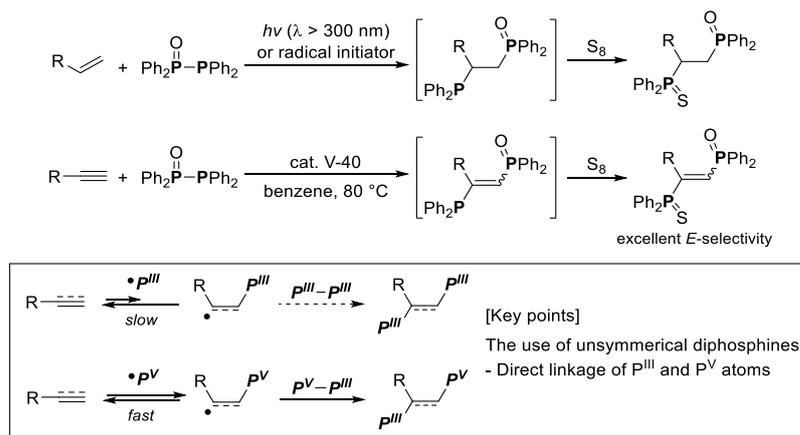
Scheme 8. Photoinduced thiophosphination of alkynes using a $(\text{PhS})_2/(\text{Ph}_2\text{P})_2$ binary system.

We next focused on the photoinduced selenophosphination and phosphinotelluration of alkynes. The results are summarized in Scheme 9. The combination of $(\text{Ph}_2\text{P})_2$ and $(\text{PhSe})_2$, or $(\text{PhTe})_2$ with alkynes, or allenes successfully provided the corresponding 1,2-adducts with excellent regio- and stereoselectivity via the formation of $\text{Ph}_2\text{P}\text{-ChPh}$ ($\text{Ch} = \text{Se}, \text{Te}$) under light. In the case of the phosphinotelluration of alkynes, the phosphorus group was introduced to the terminal position, and the PhTe -group was introduced to the internal position, in sharp contrast to thiophosphination and selenophosphination. These results clearly indicated that the relative reactivity toward unsaturated bonds could be estimated as follows: $\text{PhS}\bullet > \text{PhSe}\bullet > \text{Ph}_2\text{P}\bullet > \text{PhTe}\bullet$ [58,59].



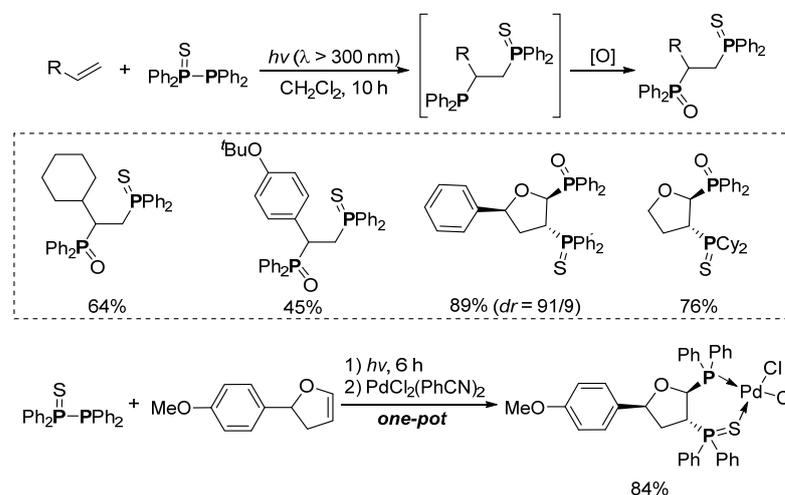
Scheme 9. Photoinduced selenophosphination and phosphinotelluration.

Although the radical addition of $(\text{Ph}_2\text{P})_2$ to alkynes and some application with the combination of dichalcogenides could be conducted, the addition reaction of $(\text{Ph}_2\text{P})_2$ to alkenes hardly proceeded in the presence of radical initiators or under photoirradiation. This might be because of the instability of the β -heteroatom-substituted alkyl radical generated from alkene compared to that of the β -heteroatom-substituted alkenyl radical generated from alkyne. In Section 2, we pointed out that the use of unsymmetric interelement bonds is very effective for the radical addition to unsaturated bonds. Thus, we selected tetraphenyldiphosphine monoxide, $\text{Ph}_2\text{P}(\text{O})\text{-PPh}_2$, as an unsymmetrical diphosphine. This diphosphine is composed of two types of phosphorus units, namely trivalent and pentavalent phosphorus groups. The higher reactivity of the pentavalent phosphorus radical compared to the trivalent one, and the higher carbon radical capturing ability of the trivalent phosphorus group compared to the pentavalent one, effectively caused the desired radical addition to alkenes [60,61]. This method could also be applied to the addition of $\text{Ph}_2\text{P}(\text{O})\text{-PPh}_2$ to alkynes, which proceeded smoothly in the presence of catalytic V-40 as the radical initiator, affording the corresponding 1-diphenylphosphinyl-2-diphenylthiophosphinyl-1-alkenes in good yields with excellent regio- and stereoselectivity ($E/Z = 95:5\text{--}99:1$) (Scheme 10) [62].



Scheme 10. Radical phosphinylphosphination of alkenes and alkynes, using tetraphenyldiphosphine monoxide as the phosphorus interelement compounds.

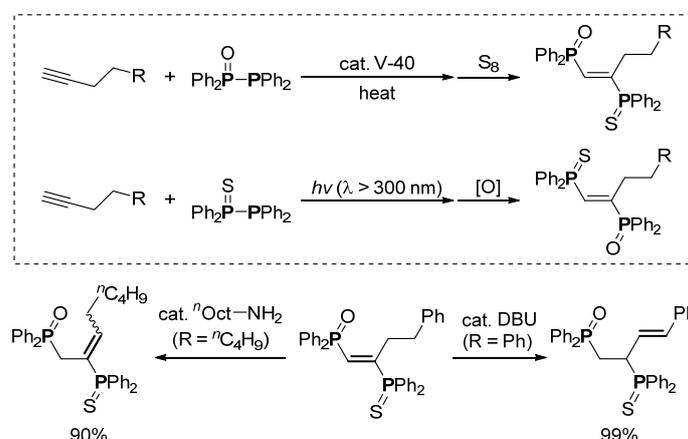
In the case of $\text{Ph}_2\text{P}(\text{O})\text{-PPh}_2$, however, the radical addition reaction required a long photoirradiation time (40 h) to obtain the adducts in adequate yields. This is because the cutoff of the absorption of $\text{Ph}_2\text{P}(\text{O})\text{-PPh}_2$ reached only 318 nm. As the result, near-UV and visible light irradiation was less effective for the homolytic cleavage of the P–P bond of $\text{Ph}_2\text{P}(\text{O})\text{-PPh}_2$. Thus, we selected tetraphenyldiphosphine monosulfide, $\text{Ph}_2\text{P}(\text{S})\text{-PPh}_2$, the absorption cutoff of which reached 345 nm. The effective reactivity of $\text{Ph}_2\text{P}(\text{S})\text{-PPh}_2$ was observed, and the corresponding *vic*-diphosphinyl adducts were obtained in good yields with a shorter photoirradiation time (10 h). This method could also be applied to the five-membered cyclic alkenes, and a one-pot reaction of the *vic*-diphosphinyl adducts (in situ-generated) with $\text{PdCl}_2(\text{PhCN})_2$ provided the corresponding Pd^{II} bisphosphane monosulfide complex in good yields (Scheme 11) [63].



Scheme 11. Photoinduced bisphosphination of alkenes, using tetraphenyldiphosphine monosulfide as the phosphorus interelement compounds.

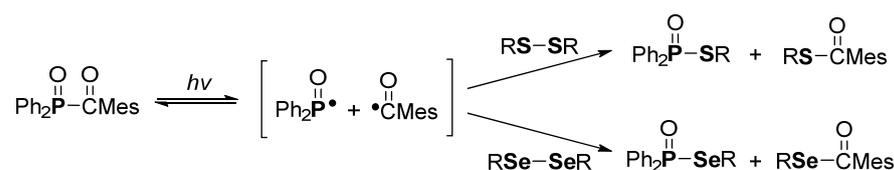
This system using $\text{Ph}_2\text{P}(\text{S})\text{-PPh}_2$ successfully worked in the case of the photoinduced bisphosphination of alkynes. In this reaction, $\text{Ph}_2\text{P}(\text{S})$ -units were introduced to terminal positions, and $\text{Ph}_2\text{P}(\text{O})$ -units were located at the internal position, in contrast to the case of $\text{Ph}_2\text{P}(\text{O})\text{-PPh}_2$. Hence, the regio-complementary introduction of $\text{Ph}_2\text{P}(\text{S})$ and $\text{Ph}_2\text{P}(\text{O})$ groups to alkynes could be attained, leading to a novel synthetic strategy for phosphine-centered functional molecules (Scheme 12). During our investigation of the further transformation of the *vic*-1,2-bisphosphinoalkenes obtained by the developed radical addition reaction of alkynes, we recently developed a novel base-catalyzed double-bond

isomerization reaction of the bisphosphinated products. A catalytic amount of primary amines or DBU successfully catalyzed the isomerization, and the novel bisphosphinated vinyl compounds were obtained with completely regio- and stereoselectivities [64].



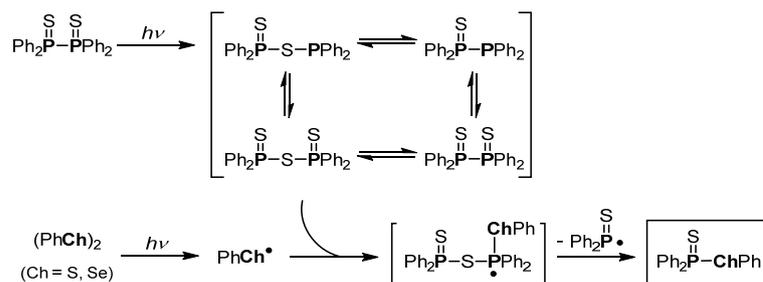
Scheme 12. Regio-complementary synthesis of *vic*-1,2-bisphosphinoalkenes and its base-catalyzed double bond isomerization.

Diphosphines, which have trivalent phosphorus groups, are moisture- and air-sensitive; therefore, the strict Schlenk technique under an inert gas atmosphere is required. For the easy handling of phosphorus interelement compounds, it is expected to be effective to use interelement compounds that do not contain trivalent phosphorus groups, or, in other words, that are composed of pentavalent phosphorus groups. From this viewpoint, we developed the preparation of various kinds of stable phosphorus-centered interelement compounds, which have pentavalent phosphorus groups. For example, a photoinduced coupling reaction of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO) with $(\text{PhCh})_2$ ($\text{Ch} = \text{S}, \text{Se}$) was reported. Under photoirradiation, the homolytic cleavage of the $\text{P}^{\text{V}}(\text{O})\text{-C}(\text{O})$ bond in TMDPO occurred to form $\text{Ph}_2\text{P}(\text{O})^\bullet$ and $\text{MesC}(\text{O})^\bullet$. Then, the formed radicals reacted with dichalcogenides via $\text{S}_{\text{H}2}$ reaction or radical coupling pathways, and the corresponding thio- or selenophosphinates and thio- or selenoesters, respectively, were obtained in excellent yields (Scheme 13) [65].



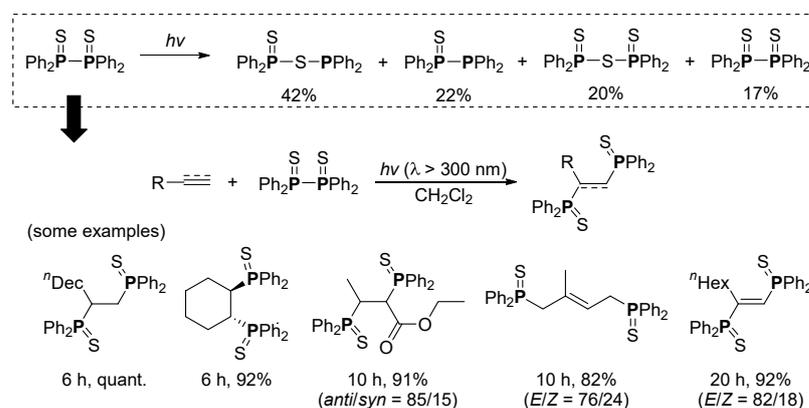
Scheme 13. Photoinduced synthesis of $\text{P}^{\text{V}}(\text{O})$ -chalcogen interelement compounds via radical generation from stable diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

Interestingly, when the photoinduced reactions of tetraphenyldiphosphine disulfide with an equivalent amount of diphenyl disulfide or diselenides, *S*- or *Se*-phenyl diphenylphosphinodithioates, respectively, were obtained in excellent yields as the sole products (Scheme 14). The mechanistic investigation revealed that the reaction proceeded via the photoinduced isomerization of tetraphenyldiphosphine disulfide, $\text{Ph}_2\text{P}(\text{S})\text{-P}(\text{S})\text{Ph}_2$, to generate an equilibrium mixture of $\text{Ph}_2\text{P}(\text{S})\text{-S-PPh}_2$, $\text{Ph}_2\text{P}(\text{S})\text{-PPh}_2$, $\text{Ph}_2\text{P}(\text{S})\text{-S-P}(\text{S})\text{Ph}_2$, and $\text{Ph}_2\text{P}(\text{S})\text{-P}(\text{S})\text{Ph}_2$. Among them, $\text{Ph}_2\text{P}(\text{S})\text{-S-PPh}_2$ mainly acted as the carbon-radical-trapping reagent at the trivalent phosphorus site (Scheme 14). The $\text{P}^{\text{V}}\text{-Ch}$ bond formation usually proceeds via ionic pathways, using air- and moisture-sensitive reagents, and there has been no example of a radical method for the preparation of $\text{P}^{\text{V}}\text{-Ch}$ bonds. Therefore, the developed method will contribute to the further utilization of phosphorus-centered interelement compounds in organic synthesis [66].



Scheme 14. Direct construction of $\text{P}^{\text{V}}\text{-Ch}$ bonds via photoinduced radical reaction with tetraphenyldiphosphine disulfide and dichalcogenides.

Furthermore, the photoinduced bisphosphination of alkenes, alkynes, and conjugate dienes, using moisture- and air-stable $\text{Ph}_2\text{P}(\text{S})\text{-P}(\text{S})\text{Ph}_2$, was developed. Upon photoirradiation, the homolysis of a $\text{P}^{\text{V}}\text{-P}^{\text{V}}$ bond occurred to generate $\text{Ph}_2\text{P}(\text{S})\cdot$, which added to the unsaturated bond. The resulting carbon radical was captured with $\text{Ph}_2\text{P}(\text{S})\text{-S-PPh}_2$ at the trivalent phosphorus site, affording the corresponding *vic*-1,2-bisphosphinoalkanes in excellent yields in a short reaction time (4–10 h) (Scheme 15) [67].



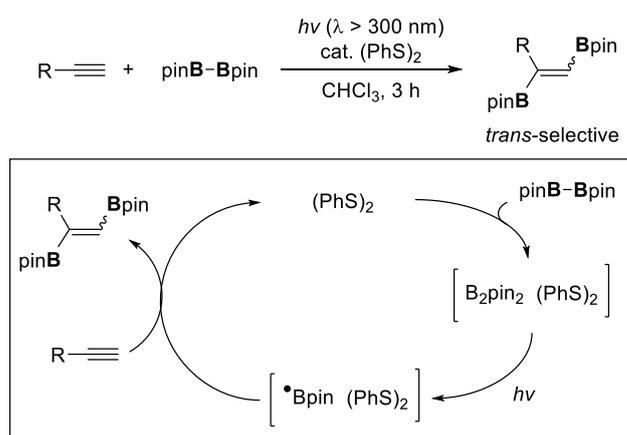
Scheme 15. Photoinduced bisphosphination using tetraphenyldiphosphine disulfide.

4. Boron-Centered Interelement Compounds in Radical Addition Reactions

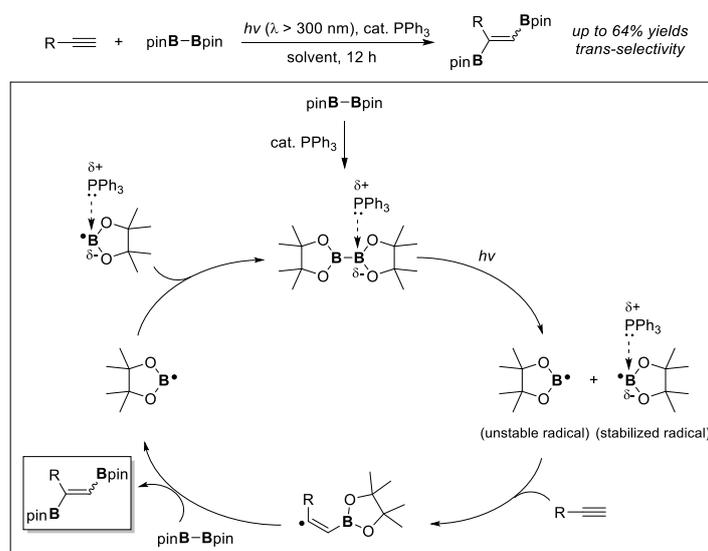
Cross-coupling reactions using boron as a coupling partner are the most important carbon-carbon bond formation method in organic synthesis and are widely used for a wide range of molecular transformations to synthesize pharmaceuticals, functional materials, etc. Along with this, the development of reactions to introduce boron functional groups into organic molecules is becoming increasingly important. Recently, there has been a strong demand for the development of green synthetic methods with high atom efficiency and low environmental impact. From this perspective, addition reactions in which all starting substrates are ideally incorporated into the product are becoming more important than substitution reactions in which leaving groups are always byproducts. Diboron (B-B), haloboron (B-X), and silylboron (B-Si) are widely used as interelement compounds containing boron, and many excellent reactions using transition metal catalysts and bases have been reported [68–74]. The value of these reactions in organic synthesis is unassailable, but on the other hand, from the standpoint of environmental compatibility, the use of stoichiometric or higher amounts of bases leads to an environmental burden, and the use of metal catalysts requires the costly removal of trace amounts of metals in the products. Therefore, the development of the “metal-free” synthesis of boron compounds is expected to become more important in the future. In this section, we review the radical addition reactions and recently developed metal-free ionic reactions of boron-containing interelement compounds.

Diborons, the interelement compounds with B–B direct linkages, have been utilized as the boron sources in many reactions [75,76]. The first example of the metal-free diboration of unsaturated compounds with X_2B-BX_2 ($X = F, Cl$) was reported in 1959 [77]. After some related works [78,79], the metal-free diboration of alkenes, an allene [80], and conjugate enones [81–83] by the activation of diborons with Lewis bases was reported by Gulyás and Fernández. In 2014, Hirano and Uchiyama reported the *trans*-diborylation of propargylic alcohols in the presence of butyllithium [84]. Furthermore, Ohmiya and Sawamura reported the phosphine-catalyzed diboration or silaboration and LiO^tBu -catalyzed diboration of electron-deficient alkynes [85,86]. After these pioneering works, there were many examples of such base-catalyzed diboration of unsaturated compounds. In these reactions, alkali metal alkoxides [87–89], amines [90–92], and butyllithium [93–96] were used as bases.

On the other hand, we reported in 2015 that the radical diboration of alkynes successfully proceeded under light in the presence of catalytic $(PhS)_2$, and the corresponding double borylation products were obtained in good yields with good *trans*-selectivity. The mechanistic investigation of the reaction by electron spin resonance (ESR) spectroscopy revealed that a novel boryl-centered radical was firstly generated (Scheme 16) [97]. Furthermore, the radical diboration of alkynes also proceeded in the presence of catalytic amount of PPh_3 instead of $(PhS)_2$, and the corresponding *vic*-diborated products were obtained in moderate yields with excellent *trans*-selectivity (Scheme 17) [98].

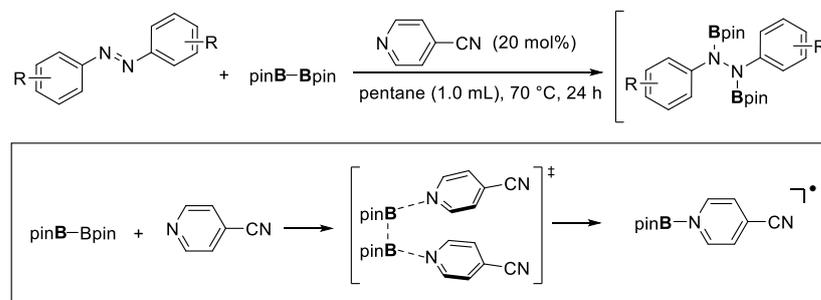


Scheme 16. Organosulfide-catalyzed photoinduced diboration of alkynes.



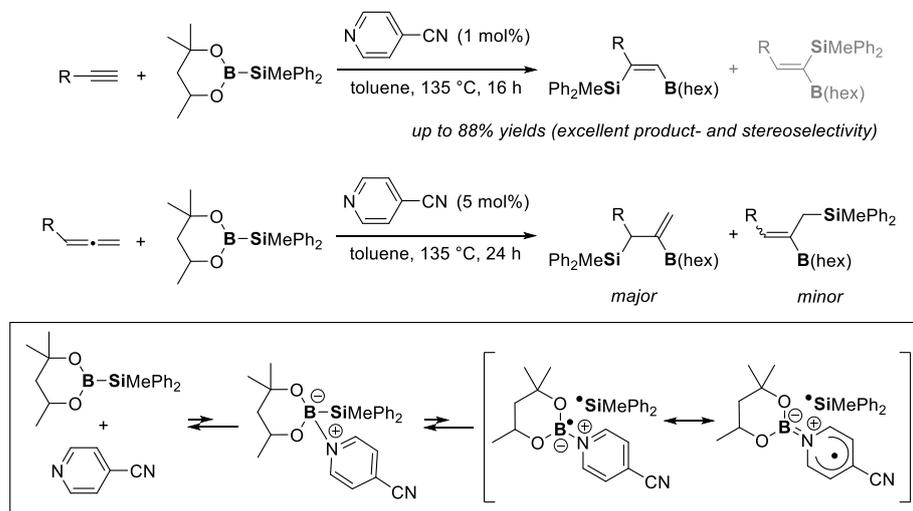
Scheme 17. PPh_3 -catalyzed photoinduced metal-free diboration of alkynes.

Zhu and Li et al. reported the homolytic cleavage of boron–boron bonds by the cooperative catalysis of Lewis bases in 2016. In this system, the addition of a catalytic amount of 4-cyanopyridine was effective, and the authors suggested that the catalyst might act as a single-electron acceptor in the homolytic cleavage of boron–boron bonds. They also demonstrated the application of this system to the catalytic reduction of azo-compounds via the radical diboration of azoarenes, and the corresponding products were obtained in good to excellent yields (Scheme 18) [99–101].



Scheme 18. Homolytic cleavage of a B–B bond, using 4-cyanopyridine as the Lewis base.

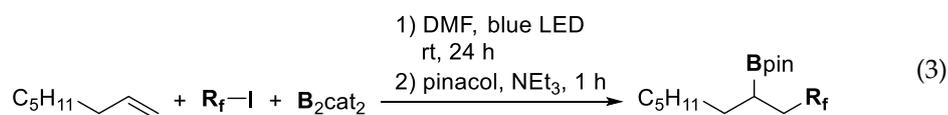
The use of 4-cyanopyridine as the catalyst is also effective for the homolytic cleavage of boron-centered interelement compounds [102]. For example, Ohmura and Sugimoto et al. reported the 4-cyanopyridine-catalyzed radical silaboration of alkynes in 2019. The B–Si bond could be activated under heat, and the corresponding boryl radical was stabilized by the catalyst. The author suggested that the generated more nucleophilic pyridine–boryl radical preferentially attacked the more electron-deficient alkyne terminal position, and the formed vinyl radical was smoothly captured by the silyl radical to form the corresponding products with excellent product- and stereoselectivity. In addition, the system could be applied to the silaboration of allenes (Scheme 19) [103–105].



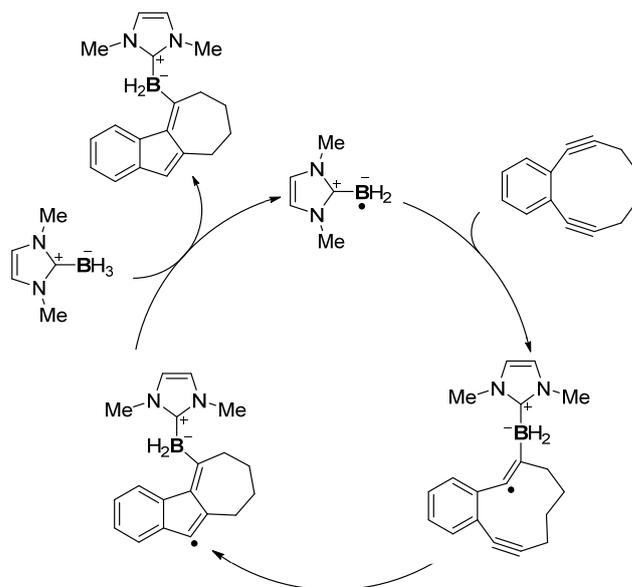
Scheme 19. 4-Cyanopyridine-catalyzed radical silaboration of alkynes and allenes.

Another approach for the introduction of boron-centered functional groups into unsaturated compounds is the use of these boryl groups in combination with other reactive radical species [106]. In 2018, Studer et al. reported the metal-free 1,2-carboboration of inactivated alkenes, using the combination of perfluoroalkyl iodides and diborons as the carbon radical precursors and carbon-radical-trapping agents, respectively (Equation (3)). Under blue LED light irradiation, the carbon-centered radical, in situ-generated via C–I

bond homolysis, first reacted with alkenes, and the formed secondary alkyl radical could be trapped with diborons to result in the corresponding adducts in good yields [107].

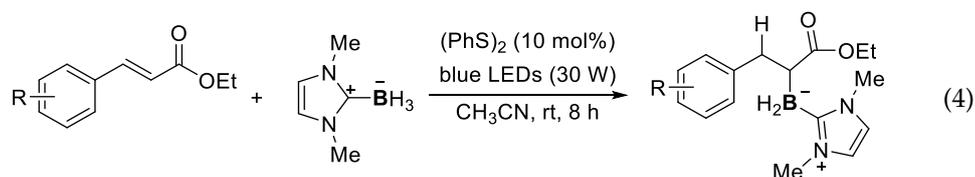


N-Heterocyclic carbene boranes (NHC-boranes) can be activated to form the corresponding NHC-boryl radicals, which can be used for radical cascade reactions [108–112]. A pioneering work of radical borylations using NHC-boranes and catalytic initiators was reported by Curran and Taniguchi et al. in 2017. In this reaction, benzo[3,4]cyclodec-3-ene-1,5-dienes, a strained cyclic diene, could be transformed to 5-borylated 6,7,8,9-tetrahydrobenzo[*a*]azulene via (1) the generation of NHC-boryl radicals from NHC-boranes by hydrogen abstraction using initiators, (2) the addition of the boryl radicals to form alkenyl radicals, (3) following transannular cyclization, and (4) a hydrogen atom transfer (HAT) reaction from the NHC-boranes (Scheme 20) [113]. The NHC-boranes/radical initiator conditions could be applied to the radical borylation/cyclization cascade of 1,6-enynes for the synthesis of boron-handled hetero- and carbocycles, which was reported by Wang et al. in 2017 [114].

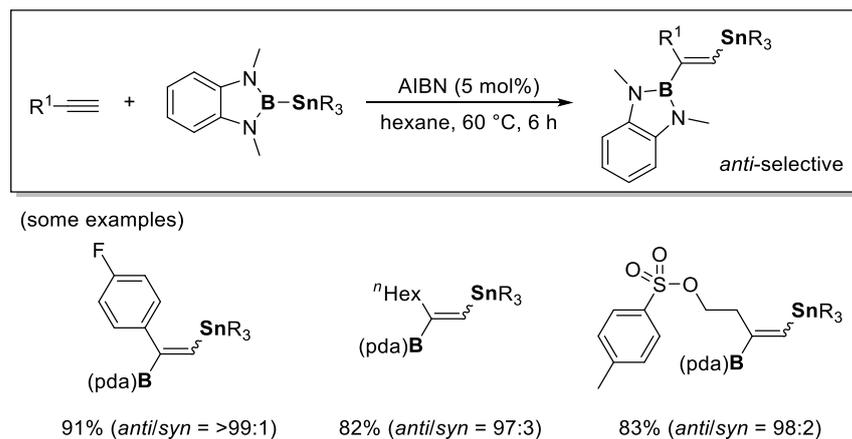


Scheme 20. Borylative radical cyclization of strained cyclic diynes using NHC-boranes.

For photoinduced radical borylation using NHC-boranes, the use of photocatalysts is also effective. In 2022, Wang et al. reported that visible light induced the regioselective hydroborylation of α,β -unsaturated carbonyl compounds with NHC-boranes, using $(\text{PhS})_2$ as the photocatalyst. This system could be conducted by blue LED light irradiation, and a variety of α -borylcarbonyl compounds could be obtained in good to excellent yields (Equation (4)) [115].



Concerning the utilization of the interelement compounds with boron–Group 14 element linkages, Nishimoro and Yasuda et al. reported in 2022 that the *anti*-selective radical borylstannylation of alkynes successfully proceeded with (*o*-phenylenediaminato)borylstannanes. The authors estimated that the vacant *p*-orbital of the boron in (*o*-phenylenediaminato)borylstannane conjugated with the orbital of the phenylenediamine structure, and the efficient delocalization lowered the energy level of the LUMO; this allowed a large interaction with the SOMO of the alkyl radical (from initiators), and the radical borylation and stannylation took place smoothly. In addition, the S_H2 reaction with generated vinyl radicals and (*o*-phenylenediaminato)borylstannane proceeded in a manner that avoided steric repulsion, and the corresponding products were obtained with *anti*-selectively (Scheme 21) [116,117].



Scheme 21. *anti*-Selective radical borylstannylation of alkynes based on the molecular design of borylstannanes.

5. Summary and Conclusions

This review focuses on the recent developments in the multi-functionalization of unsaturated compounds by radical addition reactions using interelement compounds. In recent years, radical addition reactions of interelement compounds have been energetically studied, and their environmentally benign and high atomic efficiency have attracted much attention as alternatives to transition-metal-catalyzed reactions and ionic reactions. In order to construct the important molecule scaffolds for pharmaceuticals and functional materials, the development of the precise introduction of heteroatom-centered groups has been actively pursued, focusing on the characteristic features of heteroatoms.

For the introduction of heteroatoms, compounds with heteroatom–hydrogen or heteroatom–halogen bonds have been mainly used as heteroatom sources. However, the application of various interelement compounds to radical addition reactions is more limited. For group 15 and 16 heteroatoms, the presence of (a) lone pair(s) can allow the homolysis of the interelement bonds via $n-\sigma^*$ transition induced by photoirradiation. In addition, radical addition reactions are more likely to occur in group 16 heteroatoms than in other 13–15 groups because the number of substituents is relatively small. On the other hand, with group 15 phosphorus, the number of substituents increases, so steric hindrance affects addition, and radical addition reactions are somewhat more difficult to control, because trivalent phosphorus is unstable to air and moisture. On the other hand, group 13 boron has an unoccupied orbital, so homolysis results in a five-electron radical species, which is difficult to generate and control. Thus, when a Lewis base with a lone pair is coordinated to the unoccupied orbital of boron, the radical species generated is seven-valent and can be controlled. In group 14 heteroatoms, there are no lone pairs or unoccupied orbitals, and the number of bonds is much higher, so steric hindrance is a serious problem for inducing addition. Therefore, the development of synthetic applications of these unused interelement compounds by radical reactions is expected to provide new synthetic

strategies for organic synthesis and further expand the potential of main group element organic chemistry.

We hope that the knowledge on the utilization of radical reactions of interelement compounds presented in this review will contribute to the further development of organic synthesis and green chemistry in the future.

Author Contributions: Conceptualization, Y.Y. and A.O.; writing—original draft preparation, Y.Y. and A.O.; writing—review and editing, Y.Y. and A.O.; funding acquisition, Y.Y. and A.O. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by JSPS KAKENHI Grant Numbers JP22H02124 and JP22J14638, from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Y.Y. thanks the Japan Society for the Promotion of Science for the Research Fellowship for Young Scientists.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Suzuki, A. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. *J. Organomet. Chem.* **1999**, *576*, 147–168. [[CrossRef](#)]
2. Kakiuchi, F.; Kochi, T. Transition-Metal-Catalyzed Carbon–Carbon Bond Formation via Carbon–Hydrogen Bond Cleavage. *Synthesis* **2008**, *2008*, 3013–3039. [[CrossRef](#)]
3. Achar, T.K.; Bose, A.; Mal, P. Mechanochemical synthesis of small organic molecules. *Beilstein J. Org. Chem.* **2017**, *13*, 1907–1931. [[CrossRef](#)]
4. Zheng, K.; Liu, X.; Feng, X. Recent Advances in Metal-Catalyzed Asymmetric 1,4-Conjugate Addition (ACA) of Nonorganometallic Nucleophiles. *Chem. Rev.* **2018**, *118*, 7586–7656. [[CrossRef](#)]
5. Hooshmand, S.E.; Heidari, B.; Sedghi, R.; Varma, R.S. Recent advances in the Suzuki–Miyaura cross-coupling reaction using efficient catalysts in eco-friendly media. *Green Chem.* **2019**, *21*, 381–405. [[CrossRef](#)]
6. Samanta, R.; Matcha, K.; Antonchick, A.P. Metal-Free Oxidative Carbon–Heteroatom Bond Formation Through C–H Bond Functionalization. *Eur. J. Org. Chem.* **2013**, *2013*, 5769–5804. [[CrossRef](#)]
7. Besset, T.; Poisson, T.; Pannecoucke, X. Direct Vicinal Difunctionalization of Alkynes: An Efficient Approach Towards the Synthesis of Highly Functionalized Fluorinated Alkenes. *Eur. J. Org. Chem.* **2015**, *2015*, 2765–2789. [[CrossRef](#)]
8. Chen, J.; Li, J.; Dong, Z. A Review on the Latest Progress of Chan–Lam Coupling Reaction. *Adv. Synth. Catal.* **2020**, *362*, 3311–3331. [[CrossRef](#)]
9. Usman, M.; Ren, Z.-H.; Wang, Y.-Y.; Guan, Z.-H. Recent Developments in Cobalt Catalyzed Carbon–Carbon and Carbon–Heteroatom Bond Formation via C–H Bond Functionalization. *Synthesis* **2017**, *49*, 1419–1443.
10. Beletskaya, I.; Moberg, C. Element–Element Additions to Unsaturated Carbon–Carbon Bonds Catalyzed by Transition Metal Complexes. *Chem. Rev.* **2006**, *106*, 2320–2354. [[CrossRef](#)]
11. Kawaguchi, S.-I.; Yamamoto, Y.; Ogawa, A. Catalytic synthesis of sulfur and phosphorus compounds via atom-economic reactions. *Mendeleev Commun.* **2020**, *30*, 129–138. [[CrossRef](#)]
12. Beletskaya, I.P.; Ananikov, V.P. Transition-Metal-Catalyzed C–S, C–Se, and C–Te Bond Formations via Cross-Coupling and Atom-Economic Addition Reactions. Achievements and Challenges. *Chem. Rev.* **2022**, *122*, 16110–16293. [[CrossRef](#)] [[PubMed](#)]
13. Ogawa, A. Addition of X–Y Reagents to Alkenes, Alkynes, and Allenes. In *Comprehensive Organic Synthesis II*; Elsevier: Amsterdam, The Netherlands, 2014; Volume 4, pp. 392–411.
14. Liu, L.; Ward, R.M.; Schomaker, J.M. Mechanistic Aspects and Synthetic Applications of Radical Additions to Allenes. *Chem. Rev.* **2019**, *119*, 12422–12490. [[CrossRef](#)] [[PubMed](#)]
15. Tamao, K.; Yamaguchi, S. Introduction to The Chemistry of Interelement Linkage. *J. Organomet. Chem.* **2000**, *611*, 3–4. [[CrossRef](#)]
16. Tokitoh, N. New aspects in the chemistry of low-coordinated inter-element compounds of heavier Group 15 elements. *J. Organomet. Chem.* **2000**, *611*, 217–227. [[CrossRef](#)]
17. Hayashi, T.; Matsumoto, Y.; Ito, Y. Palladium-Catalyzed Asymmetric 1,4-Disilylation of α,β -Unsaturated Ketones: Catalytic Asymmetric Synthesis of β -Hydroxy Ketones. *J. Am. Chem. Soc.* **1988**, *110*, 5579–5581. [[CrossRef](#)]
18. Lu, A.; Ji, X.; Zhou, B.; Wu, Z.; Zhang, Y. Palladium-Catalyzed, C–H Silylation through Palladacycles Generated from Aryl Halides. *Angew. Chem. Int. Ed.* **2018**, *57*, 3233–3237. [[CrossRef](#)]

19. Wollenburg, M.; Bajohr, J.; Marchese, A.D.; Whyte, A.; Glorius, F.; Lautens, M. Palladium-Catalyzed Disilylation and Digermanylation of Alkene Tethered Aryl Halides: Direct Access to Versatile Silylated and Germanylated Heterocycles. *Org. Lett.* **2020**, *22*, 3679–3683. [[CrossRef](#)]
20. Louka, A.; Stratakis, M. Synthesis of Vinylgermanes via the Au/TiO₂-Catalyzed *cis*-1,2-Digermylation of Alkynes and the Regioselective Hydrogermylation of Allenes. *Org. Lett.* **2021**, *23*, 3599–3603. [[CrossRef](#)]
21. Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Sekiguchi, M.; Kambe, N.; Sonoda, N. Photo-initiated addition of diphenyl diselenide to allenes. *Tetrahedron Lett.* **1990**, *31*, 5931–5934. [[CrossRef](#)]
22. Ogawa, A.; Yokoyama, H.; Yokoyama, K.; Masawaki, T.; Kambe, N.; Sonoda, N. Photo-initiated addition of diphenyl diselenide to acetylenes. *J. Org. Chem.* **1991**, *56*, 5721–5723. [[CrossRef](#)]
23. Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Obayashi, R.; Kambe, N.; Sonoda, N. Photo-initiated addition of diphenyl ditelluride to acetylenes. *J. Chem. Soc. Chem. Commun.* **1991**, 1748–1750. [[CrossRef](#)]
24. Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L.-B.; Kambe, N.; Sonoda, N. Photo-Induced Ditelluration of Acetylenes with Diphenyl Ditelluride. *Tetrahedron* **1993**, *49*, 1177–1188. [[CrossRef](#)]
25. Tran, C.C.; Kawaguchi, S.-I.; Sato, F.; Nomoto, A.; Ogawa, A. Photoinduced Cyclizations of *o*-Diisocynoarenes with Organic Diselenides and Thiols that Afford Chalcogenated Quinoxalines. *J. Org. Chem.* **2020**, *85*, 7258–7266. [[CrossRef](#)] [[PubMed](#)]
26. Mitamura, T.; Iwata, K.; Nomoto, A.; Ogawa, A. Photochemical intramolecular cyclization of *o*-alkynylaryl isocyanides with organic dichalcogenides leading to 2,4-bischalcogenated quinolines. *Org. Biomol. Chem.* **2011**, *9*, 3768–3775. [[CrossRef](#)] [[PubMed](#)]
27. Mitamura, T.; Iwata, K.; Ogawa, A. (PhTe)₂-Mediated Intramolecular Radical Cyclization of *o*-Ethylnylaryl Isocyanides Leading to Bistellurated Quinolines upon Visible-Light Irradiation. *Org. Lett.* **2009**, *11*, 3422–3424. [[CrossRef](#)]
28. Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. A highly selective thioselenation of olefins using disulfide-diselenide mixed system. *J. Org. Chem.* **1992**, *57*, 111–115. [[CrossRef](#)]
29. Ogawa, A.; Obayashi, R.; Ine, H.; Tsuboi, Y.; Sonoda, N.; Hirao, T. Highly Regioselective Thioselenation of Acetylenes by Using a (PhS)₂–(PhSe)₂ Binary System. *J. Org. Chem.* **1998**, *63*, 881–884. [[CrossRef](#)]
30. Ogawa, A.; Obayashi, R.; Doi, M.; Sonoda, N.; Hirao, T. A Novel Photoinduced Thioselenation of Allenes by Use of a Disulfide–Diselenide Binary System. *J. Org. Chem.* **1998**, *63*, 4277–4281. [[CrossRef](#)]
31. Ogawa, A.; Obayashi, R.; Sonoda, N.; Hirao, T. Diphenyl diselenide-assisted dithiolation of 1,3-dienes with diphenyl disulfide upon irradiation with near-UV light. *Tetrahedron Lett.* **1998**, *39*, 1577–1578. [[CrossRef](#)]
32. Ogawa, A.; Ogawa, I.; Obayashi, R.; Umezumi, K.; Doi, M.; Hirao, T. Highly Selective Thioselenation of Vinylcyclopropanes with a (PhS)₂–(PhSe)₂ Binary System and Its Application to Thiotelluration. *J. Org. Chem.* **1999**, *64*, 86–92. [[CrossRef](#)] [[PubMed](#)]
33. Tsuchii, K.; Tsuboi, Y.; Kawaguchi, S.-I.; Takahashi, J.; Sonoda, N.; Nomoto, A.; Ogawa, A. Highly Selective Double Chalcogenation of Isocyanides with Disulfide–Diselenide Mixed Systems. *J. Org. Chem.* **2006**, *72*, 415–423. [[CrossRef](#)] [[PubMed](#)]
34. Mitamura, T.; Iwata, K.; Ogawa, A. Photoinduced Intramolecular Cyclization of *o*-Ethylnylaryl Isocyanides with Organic Disulfides Mediated by Diphenyl Ditelluride. *J. Org. Chem.* **2011**, *76*, 3880–3887. [[CrossRef](#)]
35. Kim, S.; Kim, S.; Otsuka, N.; Ryu, I. Tin-Free Radical Carbonylation: Thiol Ester Synthesis Using Alkyl Allyl Sulfone Precursors, Phenyl Benzenethiosulfonate, and CO. *Angew. Chem. Int. Ed.* **2005**, *44*, 6183–6186. [[CrossRef](#)] [[PubMed](#)]
36. Zhang, M.-Z.; Ji, P.-Y.; Liu, Y.-F.; Xu, J.-W.; Guo, C.-C. Disulfides as Sulfonylating Precursors for the Synthesis of Sulfone-Containing Oxindoles. *Adv. Synth. Catal.* **2016**, *358*, 2976–2983. [[CrossRef](#)]
37. Reddy, R.J.; Kumari, A.H.; Kumar, J.J.; Nanubolu, J.B. Cs₂CO₃-Mediated Vicinal Thiosulfonylation of 1,1-Dibromo-1-Alkenes with Thiosulfonates: An Expedient Synthesis of (E)-1,2-Thiosulfonylethenes. *Adv. Synth. Catal.* **2019**, *361*, 1587–1591. [[CrossRef](#)]
38. Wang, F.; Liu, B.-X.; Rao, W.; Wang, S.-Y. Metal-Free Chemoselective Reaction of Sulfoxonium Ylides and Thiosulfonates: Diverse Synthesis of 1,4-Diketones, Aryl Sulfursulfoxonium Ylides, and β-Keto Thiosulfones Derivatives. *Org. Lett.* **2020**, *22*, 6600–6604. [[CrossRef](#)]
39. Liu, Y.; Zhang, N.; Xu, Y.; Chen, Y. Visible-Light-Induced Radical Cascade Reaction of 1-Allyl-2-ethynylbenzimidazoles with Thiosulfonates to Assemble Thiosulfonylated Pyrrolo[1,2-*a*]benzimidazoles. *J. Org. Chem.* **2021**, *86*, 16882–16891. [[CrossRef](#)]
40. Liu, X.-Y.; Tian, S.-Y.; Jiang, Y.-F.; Rao, W.; Wang, S.-Y. Visible-Light-Triggered Sulfonylation/Aryl Migration/Desulfonylation and C–S/Se Bond Formation Reaction: 1,2,4-Trifunctionalization of Butenyl Benzothiazole Sulfone with Thiosulfonate/Selenosulfonates. *Org. Lett.* **2021**, *23*, 8246–8251. [[CrossRef](#)]
41. Tamai, T.; Nomoto, A.; Tsuchii, K.; Minamida, Y.; Mitamura, T.; Sonoda, M.; Ogawa, A. Highly selective perfluoroalkylchalcogenation of alkynes by the combination of iodoperfluoroalkanes and organic dichalcogenides upon photoirradiation. *Tetrahedron* **2012**, *68*, 10516–10522. [[CrossRef](#)]
42. Kuchen, W.; Buchwald, H. Zur Kenntnis der Organophosphorverbindungen, II. Das Tetraphenyldiphosphin. *Chem. Ber.* **1958**, *91*, 2871–2877. [[CrossRef](#)]
43. Blake, A.; McQuillan, G.; Oxtan, I.; Troy, D. Diphosphine derivatives: Part VIII. Tetraphenyldiphosphine dioxide and tetraphenyldiphosphine disulphide: Structure and skeletal vibrations. Preparation of diphenylphosphine. *J. Mol. Struct.* **1982**, *78*, 265–271. [[CrossRef](#)]
44. Hirano, K.; Miura, M. Recent advances in diphosphination of alkynes and alkenes. *Tetrahedron Lett.* **2017**, *58*, 4317–4322. [[CrossRef](#)]
45. Dodds, D.L.; Haddow, M.F.; Orpen, A.G.; Pringle, P.G.; Woodward, G. Stereospecific Diphosphination of Activated Acetylenes: A General Route to Backbone-Functionalized, Chelating 1,2-Diphosphinoethenes. *Organometallics* **2006**, *25*, 5937–5945. [[CrossRef](#)]

46. Okugawa, Y.; Hirano, K.; Miura, M. Brønsted Base Mediated Stereoselective Diphosphination of Terminal Alkynes with Diphosphanes. *Org. Lett.* **2017**, *19*, 2973–2976. [[CrossRef](#)] [[PubMed](#)]
47. Okugawa, Y.; Hayashi, Y.; Kawauchi, S.; Hirano, K.; Miura, M. Diphosphination of Alkynes with Diphosphines. *Org. Lett.* **2018**, *20*, 3670–3673. [[CrossRef](#)]
48. Yorimitsu, H. Homolytic substitution at phosphorus for C–P bond formation in organic synthesis. *Beilstein J. Org. Chem.* **2013**, *9*, 1269–1277. [[CrossRef](#)]
49. Kawaguchi, S.-I.; Ogawa, A. Applications of Diphosphines in Radical Reactions. *Asian J. Org. Chem.* **2019**, *8*, 1164–1173. [[CrossRef](#)]
50. Hewertson, W.; Taylor, I.C. The reaction of tetramethyldiphosphine with butadiene. *J. Chem. Soc. C.* **1970**, 1990–1992. [[CrossRef](#)]
51. Tzschach, A.; Baensch, S. Organoarsen-Verbindungen. XVII. Zur Umsetzung von Biphosphinen und Biarsinen mit Phenylacetylen. *J. Prakt. Chem.* **1971**, *313*, 254–258. [[CrossRef](#)]
52. Otomura, N.; Okugawa, Y.; Hirano, K.; Miura, M. *vic*-Diphosphination of Alkenes with Silylphosphine under Visible-Light-Promoted Photoredox Catalysis. *Org. Lett.* **2017**, *19*, 4802–4805. [[CrossRef](#)] [[PubMed](#)]
53. Sato, A.; Yorimitsu, H.; Oshima, K. Synthesis of (E)-1,2-Diphosphanylene Derivatives from Alkynes by Radical Addition of Tetraorganodiphosphane Generated In Situ. *Angew. Chem. Int. Ed.* **2005**, *44*, 1694–1696. [[CrossRef](#)] [[PubMed](#)]
54. Kawaguchi, S.-I.; Nagata, S.; Shirai, T.; Tsuchii, K.; Nomoto, A.; Ogawa, A. Photochemical behaviors of tetraphenyldiphosphine in the presence of alkynes. *Tetrahedron Lett.* **2006**, *47*, 3919–3922. [[CrossRef](#)]
55. Shirai, T.; Kawaguchi, S.-i.; Nomoto, A.; Ogawa, A. Photoinduced highly selective thiophosphination of alkynes using a (PhS)₂/(Ph₂P)₂ binary system. *Tetrahedron Lett.* **2008**, *49*, 4043–4046. [[CrossRef](#)]
56. Wada, T.; Kondoh, A.; Yorimitsu, H.; Oshima, K. Intermolecular Radical Addition of Alkylthio- and Arylthiodiphenylphosphines to Terminal Alkynes. *Org. Lett.* **2008**, *10*, 1155–1157. [[CrossRef](#)] [[PubMed](#)]
57. Sato, A.; Yorimitsu, H.; Oshima, K. Regio- and stereoselective synthesis of 1-aryl-1-thio-2-thiophosphinylethene derivatives via a radical process. *Tetrahedron* **2009**, *65*, 1553–1558. [[CrossRef](#)]
58. Kawaguchi, S.-I.; Shirai, T.; Ohe, T.; Nomoto, A.; Sonoda, M.; Ogawa, A. Highly Regioselective Simultaneous Introduction of Phosphino and Seleno Groups into Unsaturated Bonds by the Novel Combination of (Ph₂P)₂ and (PhSe)₂ upon Photoirradiation. *J. Org. Chem.* **2009**, *74*, 1751–1754. [[CrossRef](#)]
59. Kawaguchi, S.-i.; Ohe, T.; Shirai, T.; Nomoto, A.; Sonoda, M.; Ogawa, A. Highly Selective Phosphinotelluration of Terminal Alkynes Using a (Ph₂P)₂–(PhTe)₂ Mixed System upon Visible Light Irradiation: Straightforward Access to 1-Phosphino-2-telluroalkenes. *Organometallics* **2010**, *29*, 312–316. [[CrossRef](#)]
60. Sato, Y.; Kawaguchi, S.-I.; Nomoto, A.; Ogawa, A. Highly Selective Phosphinylphosphination of Alkenes with Tetraphenyldiphosphine Monoxide. *Angew. Chem. Int. Ed.* **2016**, *55*, 9700–9703. [[CrossRef](#)]
61. Takano, H.; Katsuyama, H.; Hayashi, H.; Kanna, W.; Harabuchi, Y.; Maeda, S.; Mita, T. A theory-driven synthesis of symmetric and unsymmetric 1,2-bis(diphenylphosphino)ethane analogues via radical difunctionalization of ethylene. *Nat. Commun.* **2022**, *13*, 7034. [[CrossRef](#)]
62. Tran, D.P.; Sato, Y.; Yamamoto, Y.; Kawaguchi, S.-I.; Kodama, S.; Nomoto, A.; Ogawa, A. Highly regio- and stereoselective phosphinylphosphination of terminal alkynes with tetraphenyldiphosphine monoxide under radical conditions. *Beilstein J. Org. Chem.* **2021**, *17*, 866–872. [[CrossRef](#)] [[PubMed](#)]
63. Sato, Y.; Kawaguchi, S.-I.; Nomoto, A.; Ogawa, A. Synthesis of Bis(phosphanyl)alkane Monosulfides by the Addition of Diphosphane Monosulfides to Alkenes under Light. *Chem. A Eur. J.* **2018**, *25*, 2295–2302. [[CrossRef](#)] [[PubMed](#)]
64. Yamamoto, Y.; Tanaka, R.; Kodama, S.; Nomoto, A.; Ogawa, A. Photoinduced Bisphosphination of Alkynes with Phosphorus Interelement Compounds and Its Application to Double-Bond Isomerization. *Molecules* **2022**, *27*, 1284. [[CrossRef](#)] [[PubMed](#)]
65. Kawaguchi, S.-I.; Ogawa, A.; Sato, Y.; Nomoto, A. Photoinduced Coupling Reaction of Diphenyl(2,4,6-trimethylbenzoyl)phosphine Oxide with Interelement Compounds: Application to the Synthesis of Thio- or Selenophosphinates. *Synthesis* **2017**, *49*, 3558–3567. [[CrossRef](#)]
66. Yamamoto, Y.; Tanaka, R.; Ota, M.; Nishimura, M.; Tran, C.C.; Kawaguchi, S.-I.; Kodama, S.; Nomoto, A.; Ogawa, A. Photoinduced Syntheses and Reactivities of Phosphorus-Containing Interelement Compounds. *J. Org. Chem.* **2020**, *85*, 14708–14719. [[CrossRef](#)]
67. Sato, Y.; Nishimura, M.; Kawaguchi, S.; Nomoto, A.; Ogawa, A. Reductive Rearrangement of Tetraphenyldiphosphine Disulfide To Trigger the Bisthiophosphinylation of Alkenes and Alkynes. *Chem. A Eur. J.* **2019**, *25*, 6797–6806. [[CrossRef](#)]
68. Cuenca, A.B.; Shishido, R.; Ito, H.; Fernández, E. Transition-metal-free B–B and B–interelement reactions with organic molecules. *Chem. Soc. Rev.* **2017**, *46*, 415–430. [[CrossRef](#)]
69. Yan, G.; Huang, D.; Wu, X. Recent Advances in C–B Bond Formation through a Free Radical Pathway. *Adv. Synth. Catal.* **2017**, *360*, 1040–1053. [[CrossRef](#)]
70. Nguyen, V.D.; Nguyen, V.; Jin, S.; Dang, H.T.; Larionov, O.V. Organoboron chemistry comes to light: Recent advances in photoinduced synthetic approaches to organoboron compounds. *Tetrahedron* **2018**, *75*, 584–602. [[CrossRef](#)]
71. Friese, F.W.; Studer, A. New avenues for C–B bond formation via radical intermediates. *Chem. Sci.* **2019**, *10*, 8503–8518. [[CrossRef](#)]
72. Tian, Y.-M.; Guo, X.-N.; Braunschweig, H.; Radius, U.; Marder, T.B. Photoinduced Borylation for the Synthesis of Organoboron Compounds. *Chem. Rev.* **2021**, *121*, 3561–3597. [[CrossRef](#)] [[PubMed](#)]
73. Yadagiri, B.; Daipule, K.; Singh, S.P. Photoinduced Borylation Reactions: An Overview. *Asian, J. Org. Chem.* **2020**, *10*, 7–37. [[CrossRef](#)]

74. Lai, D.; Ghosh, S.; Hajra, A. Light-induced borylation: Developments and mechanistic insights. *Org. Biomol. Chem.* **2021**, *19*, 4397–4428. [[CrossRef](#)] [[PubMed](#)]
75. Dewhurst, R.D.; Neeve, E.C.; Braunschweig, H.; Marder, T.B. sp²–sp³ diboranes: Astounding structural variability and mild sources of nucleophilic boron for organic synthesis. *Chem. Commun.* **2015**, *51*, 9594–9607. [[CrossRef](#)]
76. Neeve, E.C.; Geier, S.J.; Mkhaliid, I.A.I.; Westcott, S.A.; Marder, T.B. Diboron(4) Compounds: From Structural Curiosity to Synthetic Workhorse. *Chem. Rev.* **2016**, *116*, 9091–9161. [[CrossRef](#)]
77. Ceron, P.; Finch, A.; Frey, J.; Kerrigan, J.; Parsons, T.; Urry, G.; Schlesinger, H. Diboron Tetrachloride and Tetrafluoride as Reagents for the Synthesis of Organoboron Compounds. II. The Behavior of the Diboron Tetrahalides toward Unsaturated Organic Compounds. *J. Am. Chem. Soc.* **1959**, *81*, 6368–6371. [[CrossRef](#)]
78. Rudolph, R.W. Mechanism of addition of diboron tetrachloride to unsaturated organic compounds. *J. Am. Chem. Soc.* **1967**, *89*, 4216–4217. [[CrossRef](#)]
79. Zeldin, M.; Gatti, A.R.; Wartik, T. Stereochemical investigations of the addition of diboron tetrachloride to unsaturated organic molecules. *J. Am. Chem. Soc.* **1967**, *89*, 4217–4218. [[CrossRef](#)]
80. Bonet, A.; Pubill-Ulldemolins, C.; Bo, C.; Gulyás, H.; Fernández, E. Transition-Metal-Free Diboration Reaction by Activation of Diboron Compounds with Simple Lewis Bases. *Angew. Chem. Int. Ed.* **2011**, *50*, 7158–7161. [[CrossRef](#)]
81. Bonet, A.; Gulyás, H.; Fernández, E. Metal-Free Catalytic Boration at the β -Position of α,β -Unsaturated Compounds: A Challenging Asymmetric Induction. *Angew. Chem. Int. Ed.* **2010**, *49*, 5130–5134. [[CrossRef](#)]
82. Pubill-Ulldemolins, C.; Bonet, A.; Bo, C.; Gulyás, H.; Fernández, E. Activation of Diboron Reagents with Brønsted Bases and Alcohols: An Experimental and Theoretical Perspective of the Organocatalytic Boron Conjugate Addition Reaction. *Chem. A Eur. J.* **2012**, *18*, 1121–1126. [[CrossRef](#)] [[PubMed](#)]
83. Pubill-Ulldemolins, C.; Bonet, A.; Gulyás, H.; Bo, C.; Fernández, E. Essential role of phosphines in organocatalytic β -boration reaction. *Org. Biomol. Chem.* **2012**, *10*, 9677–9682. [[CrossRef](#)] [[PubMed](#)]
84. Nagashima, Y.; Hirano, K.; Takita, R.; Uchiyama, M. *Trans*-Diborylation of Alkynes: *Pseudo*-Intramolecular Strategy Utilizing a Propargylic Alcohol Unit. *J. Am. Chem. Soc.* **2014**, *136*, 8532–8535. [[CrossRef](#)] [[PubMed](#)]
85. Nagao, K.; Ohmiya, H.; Sawamura, M. *Anti*-Selective Vicinal Silaboration and Diboration of Alkynoates through Phosphine Organocatalysis. *Org. Lett.* **2015**, *17*, 1304–1307. [[CrossRef](#)]
86. Morinaga, A.; Nagao, K.; Ohmiya, H.; Sawamura, M. Synthesis of 1,1-Diborylalkenes through a Brønsted Base Catalyzed Reaction between Terminal Alkynes and Bis(pinacolato)diboron. *Angew. Chem. Int. Ed.* **2015**, *54*, 15859–15862. [[CrossRef](#)]
87. Peng, S.; Liu, G.; Huang, Z. Mixed Diboration of Alkynes Catalyzed by LiOH: Regio- and Stereoselective Synthesis of *cis*-1,2-Diborylalkenes. *Org. Lett.* **2018**, *20*, 7363–7366. [[CrossRef](#)]
88. Kuang, Z.; Gao, G.; Song, Q. Base-catalyzed diborylation of alkynes: Synthesis and applications of *cis*-1,2-bis(boryl)alkenes. *Sci. China Chem.* **2019**, *62*, 62–66. [[CrossRef](#)]
89. Liu, X.; Ming, W.; Luo, X.; Friedrich, A.; Maier, J.; Radius, U.; Santos, W.L.; Marder, T.B. Regio- and Stereoselective Synthesis of 1,1-Diborylalkenes via Brønsted Base-Catalyzed Mixed Diboration of Alkynyl Esters and Amides with BpinBdan. *Eur. J. Org. Chem.* **2020**, *2020*, 1941–1946. [[CrossRef](#)]
90. Farre, A.; Soares, K.; Briggs, R.A.; Balanta, A.; Benoit, D.M.; Bonet, A. Amine Catalysis for the Organocatalytic Diboration of Challenging Alkenes. *Chem. A Eur. J.* **2016**, *22*, 17552–17556. [[CrossRef](#)]
91. Ohmura, T.; Morimasa, Y.; Suginome, M. 4,4'-Bipyridine-catalyzed Stereoselective *trans*-Diboration of Acetylenedicarboxylates to 2,3-Diborylfumarates. *Chem. Lett.* **2017**, *46*, 1793–1796. [[CrossRef](#)]
92. Gu, Y.; Duan, Y.; Shen, Y.; Martin, R. Stereoselective Base-Catalyzed 1,1-Silaboration of Terminal Alkynes. *Angew. Chem. Int. Ed.* **2020**, *59*, 2061–2065. [[CrossRef](#)] [[PubMed](#)]
93. Kojima, C.; Lee, K.-H.; Lin, Z.; Yamashita, M. Direct and Base-Catalyzed Diboration of Alkynes Using the Unsymmetrical Diborane(4), pinB-BMes₂. *J. Am. Chem. Soc.* **2016**, *138*, 6662–6669. [[CrossRef](#)] [[PubMed](#)]
94. Yukimori, D.; Nagashima, Y.; Wang, C.; Muranaka, A.; Uchiyama, M. Quadruple Borylation of Terminal Alkynes. *J. Am. Chem. Soc.* **2019**, *141*, 9819–9822. [[CrossRef](#)] [[PubMed](#)]
95. Wu, L.; Kojima, C.; Lee, K.-H.; Morisako, S.; Lin, Z.; Yamashita, M. Mechanistic study on the reaction of pinB-BMes₂ with alkynes based on experimental investigation and DFT calculations: Gradual change of mechanism depending on the substituent. *Chem. Sci.* **2021**, *12*, 9806–9815. [[CrossRef](#)]
96. Verma, A.; Snead, R.F.; Dai, Y.; Sleboznick, C.; Yang, Y.; Yu, H.; Yao, F.; Santos, W.L. Substrate-Assisted, Transition-Metal-Free Diboration of Alkynamides with Mixed Diboron: Regio- and Stereoselective Access to *trans*-1,2-Vinyldiboronates. *Angew. Chem. Int. Ed.* **2017**, *56*, 5111–5115. [[CrossRef](#)]
97. Yoshimura, A.; Takamachi, Y.; Han, L.; Ogawa, A. Organosulfide-Catalyzed Diboration of Terminal Alkynes under Light. *Chem. A Eur. J.* **2015**, *21*, 13930–13933. [[CrossRef](#)]
98. Yoshimura, A.; Takamachi, Y.; Mihara, K.; Saeki, T.; Kawaguchi, S.-I.; Han, L.-B.; Nomoto, A.; Ogawa, A. Photoinduced metal-free diboration of alkynes in the presence of organophosphine catalysts. *Tetrahedron* **2016**, *72*, 7832–7838. [[CrossRef](#)]
99. Wang, G.; Zhang, H.; Zhao, J.; Li, W.; Cao, J.; Zhu, C.; Li, S. Homolytic Cleavage of a B–B Bond by the Cooperative Catalysis of Two Lewis Bases: Computational Design and Experimental Verification. *Angew. Chem. Int. Ed.* **2016**, *55*, 5985–5989. [[CrossRef](#)]
100. Verma, P.K.; Meher, N.K.; Geetharani, K. Homolytic cleavage of diboron(4) compounds using diazabutadiene derivatives. *Chem. Commun.* **2021**, *57*, 7886–7889. [[CrossRef](#)]

101. Tsurugi, H.; Mashima, K.; Castro, L.C.M.; Sultan, I. Pyridine-Mediated B–B Bond Activation of (RO)₂B–B(OR)₂ for Generating Borylpyridine Anions and Pyridine-Stabilized Boryl Radicals as Useful Boryl Reagents in Organic Synthesis. *Synthesis* **2021**, *53*, 3211–3226. [[CrossRef](#)]
102. Xu, R.; Lu, G.-P.; Cai, C. 4-Cyanopyridine-catalyzed anti-Markovnikov selective hydroboration of alkenes. *New J. Chem.* **2018**, *42*, 16456–16459. [[CrossRef](#)]
103. Morimasa, Y.; Kabasawa, K.; Ohmura, T.; Suginome, M. Pyridine-Based Organocatalysts for Regioselective syn-1,2-Silaboration of Terminal Alkynes and Allenes. *Asian J. Org. Chem.* **2019**, *8*, 1092–1096. [[CrossRef](#)]
104. Gao, L.; Liu, X.; Li, G.; Chen, S.; Cao, J.; Wang, G.; Li, S. 1,2-Silylpyridylation Reaction of Aryl Alkenes with Silylboronate. *Org. Lett.* **2022**, *24*, 5698–5703. [[CrossRef](#)]
105. Cao, J.; Li, G.; Wang, G.; Gao, L.; Li, S. Iodoperfluoroalkylation of unactivated alkenes *via* pyridine-boryl radical initiated atom-transfer radical addition. *Org. Biomol. Chem.* **2022**, *20*, 2857–2862. [[CrossRef](#)] [[PubMed](#)]
106. Wang, D.; Mück-Lichtenfeld, C.; Studer, A. 1,*n*-Bisborylalkanes *via* Radical Boron Migration. *J. Am. Chem. Soc.* **2020**, *142*, 9119–9123. [[CrossRef](#)]
107. Cheng, Y.; Mück-Lichtenfeld, C.; Studer, A. Transition Metal-Free 1,2-Carboboration of Unactivated Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 6221–6225. [[CrossRef](#)]
108. Ueng, S.-H.; Solovyev, A.; Yuan, X.; Geib, S.J.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Newcomb, M.; Walton, J.C.; Curran, D.P. *N*-Heterocyclic Carbene Boryl Radicals: A New Class of Boron-Centered Radical. *J. Am. Chem. Soc.* **2009**, *131*, 11256–11262. [[CrossRef](#)]
109. Curran, D.P.; Solovyev, A.; Brahmi, M.M.; Fensterbank, L.; Malacria, M.; Lacôte, E. Synthesis and Reactions of *N*-Heterocyclic Carbene Boranes. *Angew. Chem. Int. Ed.* **2011**, *50*, 10294–10317. [[CrossRef](#)]
110. Kawamoto, T.; Geib, S.J.; Curran, D.P. Radical Reactions of *N*-Heterocyclic Carbene Boranes with Organic Nitriles: Cyanation of NHC-Boranes and Reductive Decyanation of Malononitriles. *J. Am. Chem. Soc.* **2015**, *137*, 8617–8622. [[CrossRef](#)]
111. Studer, A.; Curran, D.P. Catalysis of Radical Reactions: A Radical Chemistry Perspective. *Angew. Chem. Int. Ed.* **2016**, *55*, 58–102. [[CrossRef](#)]
112. Kuehn, L.; Zapf, L.; Werner, L.; Stang, M.; Würtemberger-Pietsch, S.; Krummenacher, I.; Braunschweig, H.; Lacôte, E.; Marder, T.B.; Radius, U. NHC induced radical formation *via* homolytic cleavage of B–B bonds and its role in organic reactions. *Chem. Sci.* **2022**, *13*, 8321–8333. [[CrossRef](#)] [[PubMed](#)]
113. Watanabe, T.; Hirose, D.; Curran, D.P.; Taniguchi, T. Borylative Radical Cyclizations of Benzo[3,4]cyclodec-3-ene-1,5-diynes and *N*-Heterocyclic Carbene-Boranes. *Chem. Eur. J.* **2017**, *23*, 5404–5409. [[CrossRef](#)] [[PubMed](#)]
114. Ren, S.-C.; Zhang, F.-L.; Qi, J.; Huang, Y.-S.; Xu, A.-Q.; Yan, H.-Y.; Wang, Y.-F. Radical Borylation/Cyclization Cascade of 1,6-Enynes for the Synthesis of Boron-Handled Hetero- and Carbocycles. *J. Am. Chem. Soc.* **2017**, *139*, 6050–6053. [[CrossRef](#)] [[PubMed](#)]
115. Liu, X.; Shen, Y.; Lu, C.; Jian, Y.; Xia, S.; Gao, Z.; Zheng, Y.; An, Y.; Wang, Y. Visible-light-driven PhSSPh-catalysed regioselective hydroborylation of α,β -unsaturated carbonyl compounds with NHC-boranes. *Chem. Commun.* **2022**, *58*, 8380–8383. [[CrossRef](#)] [[PubMed](#)]
116. Suzuki, K.; Nishimoto, Y.; Yasuda, M. (*o*-Phenylenediamino)borylstannanes: Efficient Reagents for Borylation of Various Alkyl Radical Precursors. *Chem. A Eur. J.* **2021**, *27*, 3968–3973. [[CrossRef](#)]
117. Suzuki, K.; Sugihara, N.; Nishimoto, Y.; Yasuda, M. anti-Selective Borylstannylation of Alkynes with (*o*-Phenylenediamino)borylstannanes by a Radical Mechanism. *Angew. Chem. Int. Ed.* **2022**, *61*, e202201883. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.