1,3-Butadiene is a useful C4 carbon source for the production of basic chemicals; but use as carbon feedstock often presents regioselectivity problems arising from its conjugated diene structure. This review summarizes the functionalization of 1,3-butadiene with carbon electrophiles by using homogeneous transition metal catalysts. A copper catalyst generated by treatment of Cu salt with alkyl Grignard reagent catalyzed internal carbon selective reductive alkylation of 1,3-butadiene with alkyl fluoride as a carbon electrophile and the alkyl Grignard reagent as a hydride source. In contrast, nickel promoted dimerization and alkylarylation of 1,3-butadiene with a similar combination of substrates. Using polyfluoroarenes as the carbon electrophiles, similar transformations proceeded to achieve the functionalization of 1,3-butadiene. The substrate scope as well as details of the reaction mechanism of these transformations are discussed.

Keywords
1,3-Butadiene, Homogeneous catalysis, Copper catalyst, Nickel catalyst, Carbon-carbon bond formation, Regioselectivity

1. Introduction

1,3-Butadiene is one of the most common C4 feedstocks and is used in large amounts for the production of polymers, such as butadiene rubber, and basic chemicals via the addition reaction. The addition reaction of molecule A-B with 1,3-butadiene creates two new bonds to form a butene with two functional groups, A and B, but controlling the regioselectivity is extremely challenging because of the conjugated structure of 1,3-butadiene\(^1\)\(^\sim\)\(^3\). Consequently, addition of A-B to 1,3-butadiene can result in three regioisomers, the 1,4-addition product 1 and two 1,2-addition products 2 and 3 (Scheme 1).

Alkylation reactions of 1,3-butadiene with alkyl electrophiles using various transition metal catalysts have been reported. Double functionalization of 1,3-dienes by alkyl halides and aldehydes was catalyzed by a Cr catalyst to form internal alkenes through the introduction of two carbon moieties at the both terminal carbons\(^6\). This reaction involved alkyl radical intermediates formed from alkyl halides. Therefore, the alkyl group attached to the terminal carbon of the 1,3-dienes via the allyl radical species. Similar transformations have been achieved by using Ti\(^5\)\(^\sim\)\(^6\), Co\(^7\), and Ni\(^9\) catalysts. However, alkylation of the internal carbon of 1,3-dienes was not possible because of the stability of the allyl radicals compared to the homoallyl radicals.

We attempted to resolve this issue with umpolung transition metal species, known as ate complexes\(^9\)\(^\sim\)\(^10\). Our strategy included the transformations of 1,3-dienes on the ate complexes to activate the 1,3-dienes as nucleophiles. The resultant allyl metal species could be trapped by carbon electrophiles, including alkyl halides, thus allowing the carbon electrophiles to attach to the internal carbons of 1,3-dienes.

Oligomerization and polymerization of 1,3-butadiene form unsaturated chemicals because of the conjugated structure, so are widely used in industrial production. Synthetic applications of 1,3-butadiene in fine chemical production depend on control of the number of 1,3-butadiene molecules incorporated into the products. Dimerization and functionalization of 1,3-butadiene, known as telomerization and discovered in 1967\(^11\)\(^\sim\)\(^12\), is
a fundamental transformation to produce C8 chemicals from two molecules of 1,3-butadiene\(^{13}\). Our strategy also allows combination of oxidative dimerization of 1,3-dienes to construct complex carbon frameworks from 1,3-dienes.

This review describes our recent achievements with the Cu- and Ni-catalyzed functionalization of 1,3-dienes.

2. Cu-catalyzed Reductive Functionalization of 1,3-Butadiene

2.1. Selective Alkylation of Internal Carbon of 1,3-Butadiene

During the course of our study on Cu-catalyzed cross-coupling reactions of alkyl halides with alkyl Grignard reagents\(^{14,15}\), we found that Cu catalyzed selective reductive alkylation of the internal carbon of 1,3-butadiene by \(n\)-octyl fluoride (5) and EtMgCl (4) to give terminal olefin 6 in 85 % yield with perfect regioselectivity (Scheme 2)\(^{16}\). In this reaction, pre-treatment of CuCl\(_2\) by EtMgCl (4) at 50 °C for 10 min was essential to achieve the selective reductive alkylation, as a mixture of 6 and the cross-coupling product decane was obtained without pre-treatment. Deuterium experiments revealed that the hydrogen atom attached to the terminal carbon of 1,3-butadiene originated from the Grignard reagent, suggesting that \(\beta\)-hydrogen elimination of alkyl copper intermediate and subsequent hydrocupration occurred rather than carbomagnesiation\(^{17}\).

Alkyl fluorides were the best alkylating reagents among the alkyl (pseudo)halides tested\(^{18,19}\). Alkyl chlorides underwent reduction and dehydrochlorination, whereas alkyl bromides and iodides afforded a complex mixture probably due to radical formation. Alkyl sulfonates could also be used as alkylating reagents but only achieved low yields (Scheme 3). Scheme 4 shows the substrate scope of alkyl fluorides. The reaction proceeded smoothly with various alkyl fluorides bearing functional groups such as ethers (8), acetals (9), C(sp\(^2\))=X bonds (X=F, Cl) (10 and 11), and a heteroarene (12). The reaction selectively occurred at the conjugated diene moiety of 1,3-butadiene even in the presence of terminal C=C double and internal C=C triple bonds to afford the corresponding products 13 and 14 in 82 % and 89 % yields, respectively.

Interesting regioselectivity outcomes were observed for substituted 1,3-dienes. Isoprene (15) with a Me group on the internal carbon underwent hydroalkylation reaction at the less hindered C=C double bond to afford 16 in 76 % yield along with a small amount of a regioisomer. In contrast, the disubstituted internal C=C double bond of 1,3-pentadiene (17) was selectively alkylated to give 18 albeit less efficiently (Scheme 5). Unfortunately, the reaction was not applicable to disubstituted 1,3-dienes.

Possible reaction pathways are illustrated in Scheme 6. The actual structure of the catalytic active species remains unclear, but treatment of Cu salt with EtMgCl at 50 °C affords a new copper species, which forms complex 20 with EtMgCl, and \(\beta\)-hydrogen elimination of 20 generates anionic Cu-H species 21. Addition of the Cu-H bond to 1,3-butadiene generates anionic allyl copper intermediates 22 and 23, which are in equilibrium. Subsequently, the formed allyl copper 23 reacts with alkyl fluorides at the \(\gamma\)-carbon of the allyl moiety to give the product 20. Alternatively, allylic Grignard reagent 24 arising from complexes 22 or 23 reacts with alkyl fluorides. Experimental evidences

\[ \text{Scheme 2 Cu-catalyzed Hydroalkylation of 1,3-Butadiene by } n-\text{OctF and EtMgCl} \]

\[ \text{Scheme 3 Effect of the Leaving Group} \]

\[ \text{Scheme 4 Scope of Alkyl Fluorides in the Cu-catalyzed Hydroalkylation Reaction} \]

\[ \text{Scheme 5 Reaction of Substituted 1,3-Dienes} \]
for the mechanism are as follows: (i) a neutral copper hydride species, Stryker reagent, did not react with a 1,3-diene; whereas addition of a Grignard reagent, PhCH₂MgBr, to the reaction accelerated the hydrocupration (21 to 22 and 23), (ii) neutral butenyl copper was inert toward alkyl fluorides, but addition of EtMgCl afforded the product (23 to 19 or 24), and (iii) butenyl-magnesium chloride reacted with alkyl fluorides to give the same product (24 to product). Kinetic study and the kinetic isotope effect implied that the reaction of complex 19 with EtMgCl is the rate-determining step in the catalytic cycle.

2.2. Hydroperfluoroarylation of 1,3-Butadiene

Perfluorinated arenes are important in many fields of material science due to their unique properties including high metabolic stability, low lowest unoccupied molecular orbital (LUMO) energies, and unique interactions with electron rich aromatic rings and polar bonds. However, the synthetic methodology of perfluoroarene compounds is not well understood. An elegant coupling reaction of pentafluorobenzene with 1,3-butadiene in the presence of a Ni catalyst involves insertion of the 1,3-butadiene into the acidic C-H bond of pentafluorobenzene. To access a wide range of perfluoroarene compounds, we investigated the C-F bond functionalization of perfluoroarenes based on the easy accessibility of perfluoroarenes in comparison to partially fluorinated arenes.

Perfluoroarene 25 was used in the Cu catalysis instead of alkyl fluorides and found that a similar coupling reaction of 25 with 1,3-butadiene occurred to give a mixture of 26 and 27 in 88 % combined yield under slightly modified conditions. Position selectivity of the monosubstituted pentafluorobenzene was almost perfect with the substitution at the para-position (Scheme 7). The reaction was sensitive to the electronic state of the perfluoroarene ring (Scheme 8). The reaction with hexafluorobenzene proceeded at 0 °C to give 28 and 29 in 60 % combined yield with 68 : 32 ratio. Conversely, the reaction with pentafluoroanisole was sluggish, and the regioselectivity was almost a 1 : 1 ratio. Position selectivity of 30 and 31 was as low as p : m : o = 50 : 40 : 6, because the MeO group acts as an electron-donating group toward the para-position but as an electron-withdrawing group toward the meta-position. Perfluoroarenes with phenyl and thienyl groups predominantly underwent the reaction at the para-position. Electron-withdrawing groups such as Cl and CF₃ greatly affected the yield of products due to the facilitated direct substitution of EtMgCl toward electron-deficient perfluoroarenes.
3. Ni-catalyzed Dimerization and Functionalization of 1,3-Butadiene

3.1. Dimerization and Alkylarylation of 1,3-Butadiene

Nickel(0) catalyzes the dimerization of 1,3-butadiene to form octadienediylnickel intermediates \(\text{40 and 41}^{30}\). This dimerization process is used for the production of cyclic dimers of 1,3-butadiene such as 1,5-cyclooctadiene \(\text{42}^{140}\). Trapping of the octadienediyl moiety on Ni may be useful to form complex molecules incorporating two 1,3-butadiene molecules but this possibility is not well characterized. Multicomponent coupling of ketones with two molecules of 1,3-butadiene occurs in the presence of \(\text{Et}_3\text{Al}^{31}\) as hydride source. Subsequently, four-component coupling reaction of ketones, two molecules of 1,3-butadiene, and \(\text{Me}_2\text{Zn}^{32}\) was reported. However, these reactions are not likely to occur with the octadienediylnickel complexes \(\text{40 and 41}^{33}\). Indeed, using aldehydes instead of ketones, a compound \(\text{44}^{(n=1)}\) incorporating only one 1,3-butadiene molecule was produced from \(\text{43}^{189}\). The number of 1,3-butadiene molecules incorporated is difficult to control, because oxidative cyclization of the carbonyl compound with 1,3-butadiene forms oxanickelacycle \(\text{43}^{89}\) instead of octadienediylnickel complexes \(\text{40 and 41}\) in these reactions. Direct trapping of the octadienediyl moiety on Ni was achieved using silyl chlorides as electrophiles, but the use of carbon electrophiles as coupling partners has not been reported.

To elucidate the reactivity of the octadienediyl moiety on Ni, we initially synthesized the Ni complex \(\text{40(L=PCy}_3^{35}\) by treating \(\text{Ni(cod)}_2\) with 1,3-butadiene and \(\text{PCy}_3^{35}\) as the ligand and identified the complex by X-ray crystallography. Although the Ni complex carries essentially the nucleophilic \(\sigma\)-allyl moiety, the complex was inert toward \(\text{n-OctF}^{}^{19}\) and \(\text{C}_6\text{F}_6\) at ambient temperature (Scheme 10). To introduce the carbon moiety into the octadienediyl moiety, we thought that the conversion of the neutral complexes \(\text{40 and 41}^{33}\) into ate complex \(\text{45}^{33}\) may increase the nucleophilicity toward carbon electrophiles (Scheme 9). Therefore, we screened reaction conditions using catalytic amounts of \(\text{NiBr}_2(\text{dme})^{36,37}\) and found that treatment of 1,3-butadiene by \(\alpha\)-\(\text{ TolMgBr}^{47}\) and \(\text{n-OctF}^{(5)}\) afforded the four-component coupling product \(\text{48}^{87}\) in 87 % yield (Scheme 11), and products incorporating one molecule of 1,3-butadiene were not observed at all.

We investigated the scope of Grignard reagents under these optimized conditions (Scheme 12). The reaction proceeded smoothly with aryl Grignard reagents carrying \(\text{Et}^{(49)}\) and \(\text{i-Pr}^{(50)}\) groups at the \(\text{ortho}\)-position. Furthermore, the sterically hindered ortho-disubstituted aryl Grignard reagent \(\text{51}^{33}\) gave the corresponding four-component coupling product in 90 % yield. In contrast, the sterically less hindered \(\text{p-FC}_6\text{H}_4\text{MgBr}^{(52)}\) resulted in lower yield of 48 %, even in the presence of 10 mol% Ni catalyst, because of the direct cross-coupling reaction of \(\text{n-OctF}^{}\) with Grignard reagent \(\text{52}^{}\) to give \(\text{53}^{37}\) in 37 % yield. These results indicated that ortho-substituent(s) are important in selectively achieving the four-component coupling reaction (vide infra). Various aryl Grignard reagents \(\text{54-57}^{58}\) with an ortho-methyl group and functionalities at the \(\text{para}\)-position selectively underwent the four-component coupling reaction in good to excellent yields. The C(\(sp^3\)-\text{F} and \(\text{-Cl bonds in the Grignard reagents \(\text{54 and 55}^{54}\) did not participate in the reaction, and the C(\(sp^3\)-\text{F bond was selectively cleaved. To demonstrate functional group tolerance, we co-
ducted the reaction with various alkyl fluorides as shown in Scheme 13. 11-Fluoro-1-undecene (58) underwent the four-component coupling reaction with 2,6-dimethylphenyl Grignard reagent (51) to give the corresponding product in 91% yield without loss or isomerization of the terminal C=C double bond. Some versatile protecting groups of hydroxy groups such as tetrahydropyranyl (59) and silyl (60) ethers remained intact. Alkyl fluorides bearing Ts (62) and Boc (63) amide moieties afforded the corresponding products in 94% and 89% yields, respectively. The four-component coupling reaction selectively occurred at the C(sp<sup>3</sup>)F bond, and the C(sp<sup>3</sup>)Cl bond in alkyl fluoride 64 as well as the C(sp<sup>2</sup>)F and Cl bonds in alkyl fluorides 65 and 66 were all tolerated under the reaction conditions. Using isoprene (15) instead of 1,3-butadiene, the four-component coupling reaction proceeded to give 67 as a mixture of four regioisomers in 76% total yield (Scheme 14).

To investigate the reaction mechanism, we conducted stoichiometric reactions (Scheme 15). In the presence of n-OctF (5) (1.1 equiv.) and 1,3-butadiene (6 equiv.), Ni(II) salt was treated with 2 equiv. of o-TolMgBr (47) to reduce Ni(II) to Ni(0), which should react with two molecules of 1,3-butadiene to form neutral octadienediylnickel intermediate, but only 14% of 5 was consumed. In contrast, the reaction with 3 equiv. of 47 did proceed to give 48 in 75% yield. These results suggest that the neutral octadienediylnickel intermediate is inert toward alkyl fluorides, and that the actual catalytic active species at the C-F bond cleavage is an ate complex generated by the reaction of neutral complex with 1 equiv. of the Grignard reagent.

Nuclear magnetic resonance (NMR) experiments supported the formation of the ate complex by treating Ni(cod)<sub>2</sub> with 1,3-butadiene and p-FC<sub>6</sub>H<sub>5</sub>MgBr (52). The octadienediyli moiety of the ate complex appeared as non-symmetric on the <sup>1</sup>H NMR spectrum, suggesting the η<sup>1</sup>:η<sup>3</sup>-coordination mode. NMR analysis confirmed formation of the ate complex, but the isolation of the ate complex was unsuccessful due to the low stability and low crystallinity. To improve the crystallinity of the ate complex, aryl lithium 68 was employed instead of the Grignard reagent, and we finally succeeded in determining the molecular structure of the ate complex 69 by X-ray crystallography (Scheme 16). As assumed, the octadienediyli moiety had coordinated to the anionic Ni center in η<sup>1</sup>:η<sup>3</sup>-mode with square-planar geometry including the aryl group.

The proposed catalytic cycle is shown in Scheme 17. The Ni precatalyst is initially reduced to Ni(0) 70 by the Grignard reagent, and then undergoes reversible oxidative dimerization of two molecules of 1,3-butadiene<sup>38</sup>~<sup>40</sup>. The neutral complex 71 reacts with aryl...
Grignard reagent to form ate complex 72 which can react with alkyl electrophiles at the Ni center and the γ-carbon of the σ-allyl moiety to give the cross-coupling and four-component coupling products, respectively. Kinetic study revealed that reaction of 72 with alkyl fluorides is the rate-determining step for each reaction pathway\(^{73}\). Therefore, the selectivity is determined at this step. Reaction of the Ni center of 72 with alkyl fluorides causes the cross-coupling reaction through Ni(IV) intermediate 74 and regenerates neutral Ni complex 71. Reaction of the γ-carbon of the σ-allyl moiety of 72 forms Ni(II) intermediate 73, which then undergoes subsequent reductive elimination to yield the four-component coupling product and regenerate Ni(0) 70.

The effect of the ortho-substituent(s) can be explained by the molecular structure of ate complex 72. The ortho-substituted aryl group binds orthogonally to the square-planar Ni plane, and the ortho-substituent(s) covers the Ni center to prevent the approach of alkyl fluorides. In contrast, the γ-carbon of the σ-allyl moiety is open for alkyl fluorides. Therefore, the reaction takes place at the γ-carbon of the σ-allyl moiety to give the four-component coupling products. However, the crystal structure of the corresponding Ph complex indicated that the dihedral angle between the Ni plane and Ph ring is only 43°, so that the Ni center is open for alkyl fluorides\(^{73}\).

Kinetics of reactions using para-substituted aryl Grignard reagents implied that both reaction pathways are accelerated by electron-donating groups, but the cross-coupling reaction is accelerated more efficiently. This result agrees well with the nucleophilic substitution mechanisms of each reaction pathway.

The reaction mechanism shown in Scheme 17 and these steric and electronic effects of aryl Grignard reagents are supported by theoretical calculations\(^{76}\), which provided unique insight into the mechanistic aspects of the Ni catalysis. At the transition state from 72 to 73, the magnesium cation coordinates to the fluorine atom in alkyl fluorides to activate the C-F bond, and the γ-carbon of the σ-allyl moiety on Ni concurrently attacks the carbon from the opposite side. This pre-association mechanism of the C-F bond with the counter cation is consistent with the experimentally determined activation parameters, which indicate that the reaction is mainly controlled by enthalpy factors\(^41\).

### 3.2. Dimerization and Perfluoroarylation of 1,3-Butadiene

Perfluoroarenes could be used in the Ni-catalyzed reaction as electrophiles instead of alkyl fluorides, but the competing direct coupling reaction with aryl Grignard reagents was slow, even for aryl Grignard reagents without ortho-substituents. For example, the four-component coupling reaction of hexafluorobenzene (75), \(p\)-FC\(_6\)H\(_4\)MgBr (52), and two molecules of 1,3-butadiene occurred in the presence of 10 mol% of NiCl\(_2\) and PPh\(_3\) at 30 °C for 3 h to form the four-component coupling product 76 in 92 % yield (Scheme 18)\(^{82}\). However, 1 equiv. of monophosphine ligand to Ni was essential to achieve the reaction efficiently, and the use of excess \(p\)-FC\(_6\)H\(_4\)MgBr (52) reduced the yield of 76 due to overreaction. Similar oxidative dimerization is known for other group 10 metals, but no reaction occurred with PdCl\(_2\) and PtCl\(_2\) as catalysts.

We tested various aryl Grignard reagents for the four-component coupling reaction under the optimized reaction conditions (Scheme 19). Phenyl Grignard reagent 77 reacted with hexafluorobenzene (75) and 1,3-butenes to give the corresponding product in 77 % yield. The reaction was not affected by substituents at the para-, meta-, and ortho-positions (78-82), and formed the corresponding four-component coupling products in good yields. Disubstituted aryl Grignard reagents 55 and 57 also reacted to give good yields.

Scheme 20 shows the scope of the four-component coupling reaction with respect to perfluoroarenes. Monosubstituted perfluoroarenes include three isomers with para-, meta-, and ortho-substitution, and the percent selectivity is indicated. Reaction of pentafluorotoluene (83) occurred at the 96 % position selectivity to afford the para-substituted product with meta-substituted product in 4 % position selectivity to give the products in 81 % total yield. In contrast, reaction of pentafluorobenzene (84) resulted in low position selectivity. The present Ni catalyst selectively cleaved the C-F bond even in the presence of C-SMe, C-Cl, and C-OTs bonds, which often act as reacting sites for Ni catalysis, with...
the other bonds remaining intact. Reaction of octafluorotoluene (88) involved the aromatic C-F bond rather than the benzylic C-F bond. Perfluoroarenes with coordinating sites such as diphenylphosphino (90) and 2-pyridyl (91) moieties reacted at the para-position. In contrast, competing direct substitution of the Grignard reagent took place at the ortho-position of the pyridyl moiety. This difference implies the intermediacy of tetracoordinate Ni complexes. π-Extended octafluoronaphthalene (92) and a biaryl (93) also participated in the reaction. Reaction occurred preferably at 2-position in the former.

3.3. Dimerization and Hydroperfluoroarylation of 1,3-Butadiene

EtMgCl acts as the hydride source in the Cu-catalyzed hydroalkylation and hydroperfluoroarylation of 1,3-dienes, as mentioned in Section 2. Therefore, we examined the use of alkyl Grignard reagents instead of aryl Grignard reagents in the Ni catalysis.

Treatment of hexafluorobenzene (75) with n-BuMgCl (94) and 1,3-butadiene in the presence of NiCl₂ (5 mol%) and PPh₃ (5 mol%) formed 1,7-octadiene 95 with the perfluorophenyl group at the 3-position in 92 % yield (Scheme 21)⁴³. The phosphine ligand was essential to this reaction, as no reaction took place in the absence of PPh₃. PPh₃ was the best ligand for the reaction among the phosphine ligands examined.

Use of the isobutyl Grignard reagent provided 95 in a comparable yield. Secondary alkyl Grignard reagents such as 2-butyl and cyclohexyl Grignard reagents also promoted the reaction, albeit less efficiently. In contrast, t-BuMgCl resulted in the formation of the direct coupling product t-BuC₆F₅ in 11 % yield, and 75 remained mostly unchanged. Using the methyl Grignard reagent (96), a four-component coupling product 97 was obtained in 50 % yield (Scheme 21).

Reaction of isoprene (15) afforded the corresponding product 98 as a mixture of four regioisomers in 46 % combined yield along with 12 % of cyclized product 99 (Scheme 22). On the other hand, 1,3-pentadiene did not react at all.

The reactivity of various perfluoroarenes and their position-selectivity were essentially the same as for previously mentioned perfluoroarylarylation (Scheme 20). Competitive reaction of hexafluorobenzene (75) with more electron rich pentafluorotoluene (83) afforded the corresponding products 95 and 100 in 80 % and 2 % yields, respectively (Scheme 23). This result is consistent with the SNAr mechanism.

The proposed catalytic cycles of the multicomponent coupling reaction of perfluoroarenes with 1,3-butadiene are shown in Scheme 24. The reaction is triggered by reduction of the Ni(II) precatalyst by the Grignard reagents. The resultant Ni(0) 101 undergoes irreversible oxidative dimerization of 1,3-butadiene to form octadienediylnickel complex 71, which is in equilibrium.
with the phosphine coordinated complex 102. Reaction of 71 with the Grignard reagent leads to formation of the ate complex 103. The anionic charge on Ni causes higher nucleophilicity, for 103 compared to neutral complexes, so 103 reacts with perfluoroarenes at the γ-carbon of the α-allyl moiety through an SNAr mechanism. Two reaction pathways are possible depending on the combination of the substrates. In the case of aryl Grignard reagents and alkyl Grignard reagents with no β-hydrogen, complex 104 undergoes reductive elimination to give the four-component coupling products. If the alkyl group with β-hydrogen attaches to complex 105, β-hydrogen elimination predominates resulting in hydroperfluoroarylation through hydride complex 106. Cyclization observed in the reaction using isoprene (15) and n-BuMgCl proceeds through insertion of the C-C double bond into the Ni-allyl moiety of 105 and subsequent reductive elimination. We conducted the following experiments to investigate the mechanism. Neutral complex 102 (PCy3 instead of PPh3) and anionic complex 103 (R = Ph and 2,6-dimethylphenyl) were isolated, and their structures determined by X-ray crystallography. Complex 102 was inert to hexafluorobenzene, whereas the ate complex generated in-situ from the Grignard reagent reacted with hexafluorobenzene to form the four-component coupling product in 82 % yield. This result clearly shows the intermediacy of the ate complex 103 in the SNAr reaction with perfluorobenzene. This step was found to be a relatively fast process in both perfluoroarylarylation and hydroperfluoroarylation. Detailed kinetic study using n-BuMgCl in a flow reactor system suggested that ate complex formation is the rate-determining step and both n-BuMgCl and neutral complex 71 form equilibria with the aggregated forms and the phosphine coordinated form 102, respectively. Kinetics with different phosphine/nickel ratios revealed that the 1:1 ratio is optimum for the hydroperfluoroarylation reaction, and higher phosphine/nickel ratio reduced the reaction rate. On the other hand, the reaction did not proceed in the absence of the phosphine ligand. Therefore, the phosphine ligand may stabilize Ni(0) intermediates 101 as well as complex 71. The observed position selectivity of monosubstituted perfluoroarenes could be explained by the electron density at the reacting carbon as the reaction preferred electron-deficient carbon. Natural bond orbital (NBO) population analysis of substrates as well as Hammett constants of the substituents are in good agreement with the position selectivity outcomes43).

4. Summary

This review describes Cu- and Ni-catalyzed functionalization of 1,3-butadiene by carbon electrophiles. Combination of a Cu catalyst and alkyl Grignard reagents could activate 1,3-butadiene as a nucleophile through hydrocupration. In contrast, Ni catalyst converted 1,3-butadiene into the dimer which was activated as a nucleophile. Alkylation of 1,3-butadiene depends on the use of alkyl fluorides as the alkylating reagent because these reagents do not generate the corresponding alkyl radicals via homolytic cleavage of the C-F bond. The Cu catalyst enabled the internal carbon selective alkylation reaction to form branched terminal olefins. The Ni catalyst allowed a new method to construct the 1,6-octadiene framework with alkyl and aryl moieties at the 3- and 8-positions, respectively, via the formation of three C-C bonds in single operation. These transformations were applicable to the coupling reaction of 1,3-butadiene with perfluoroarenes. These reactions are the first examples of the multicomponent coupling reaction of perfluoroarenes. Mechanistic studies revealed that the key intermediates at the C-F bond cleavage are the ate complexes, which carry anionic charge on the transition metals. Both the anionic transition metal center and counter cation are important in the C-F bond cleavage. The present results together with other known catalytic transformations via ate-complex-mediated C-F47,48, C-O49), and C-S bond cleavage suggest ate complexes are promising catalytic intermediates for organic synthesis.

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要 旨

炭素求電子剤を用いた1,3-ブタジエンの触媒的官能基化手法

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1,3-ブタジエンは安価かつ反応性に富むC4炭素資源として基幹化成品の製造に利用されている。しかし、反応原料として1,3-ブタジエンを利用するためには、その共役した二つの二重結合に対する付加反応の制御が重要となる。本総説では、1,3-ブタジエンの内部炭素選択的なアルキル基導入反応の発見に端を発する、均一系遷移金属錯体触媒を利用した炭素求電子剤による1,3-ブタジエンの官能基化反応に関する我々の研究成果を紹介する。鋼触媒の調製方法を工夫することにより、フッ化アルキルを炭素求電子剤、アルキルグリニャール試薬をヒドラジン源とする1,3-ブタジエンの内部炭素選択的な還元的アルキル化反応が進行することを見出した。ニッケル触媒を用いる類似の反応では、1,3-ブタジエンの二量化を伴った官能基化が可能であった。炭素求電子剤としてフッ化アルキルを用いることが、成功の鍵である。炭素求電子剤としてポリフルオロアレーンを用いた類似の反応により、1,3-ブタジエンへのポリフルオロアリール基の導入が可能である。これらの反応の基質適用範囲および反応機構に関する検討についても併せて述べる。