

Multicomponent Reactions

Deutsche Ausgabe: DOI: 10.1002/ange.201601126
Internationale Ausgabe: DOI: 10.1002/anie.201601126

Nickel-Catalyzed Dimerization and Alkylarylation of 1,3-Dienes with Alkyl Fluorides and Aryl Grignard Reagents

Takanori Iwasaki,* Xin Min, Asuka Fukuoka, Hitoshi Kuniyasu, and Nobuaki Kambe*

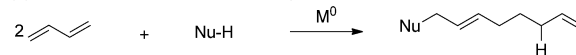
Abstract: In the presence of a nickel catalyst, 1,3-butadiene undergoes selective dimerization and alkylarylation with alkyl fluorides and aryl Grignard reagents to give 1,6-octadienes with alkyl and aryl groups at the 3- and 8-positions, respectively, by the consecutive formation of three carbon–carbon bonds. The formation of an anionic nickel complex plays an important role in forming C–C bonds with alkyl fluorides.

Multicomponent reactions provide strategically challenging and synthetically useful methods for constructing unique carbon frameworks from relatively simple molecules.^[1] 1,3-Butadiene is an important four-carbon feedstock in the chemical industry and is widely used in huge amounts, mainly for producing oligomerization and polymerization products. In terms of synthetic applications of 1,3-butadiene in fine chemistry based on its selective functionalization, many efforts have been devoted to the transition-metal-catalyzed telomerization reaction since its discovery in 1967.^[2a,b] This transformation proceeds via bis(π -allyl)metal intermediate **A**, which reacts with nucleophiles to give rise to octadienes with the concomitant introduction of a functional group (Scheme 1a).^[2] When CO or CO₂ were employed, a carboxyl group was produced.^[3]

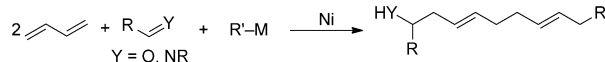
It has also been reported that the combined use of ketones, aldehydes, or imines with organozinc or -aluminum reagents enables the bifunctionalization of both terminal carbon atoms of octadienes via metallacycle intermediates (Scheme 1b).^[4] This reaction provides a useful method for introducing two different carbon moieties into the 2,6-octadiene framework, although the three-component coupling of these reagents in a 1:1:1 ratio competes or even occurs preferentially in some cases.^[4a,c]

We previously reported on the dimerization and arylsilylation^[5] or disilylation^[6] of 1,3-butadiene with chlorosilanes as the electrophile in the presence of a Ni or Pd catalyst, respectively (Scheme 1c). This reaction is promoted by Grignard reagents, which enable the formation of an anionic nickel complex **B** as the catalytically active species. However, the use of a simple alkyl electrophile, such as an alkyl halide, in this transformation has not yet been achieved, mainly

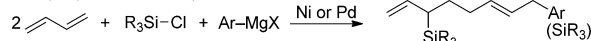
(a) Reactions with heteroatom nucleophiles



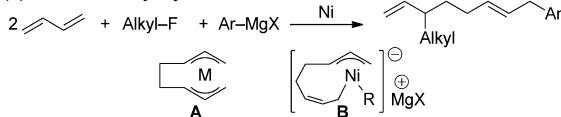
(b) Reactions with heteroatom-containing electrophiles and organometallics



(c) Arylsilylation and disilylation



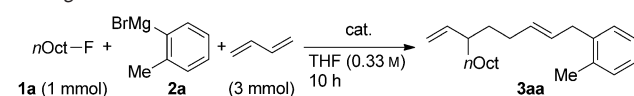
(d) This work: alkylarylation



Scheme 1. Dimerization and functionalization of 1,3-butadiene.

because of the rapid direct cross-coupling between alkyl halides and organometallic reagents.^[7–9] We herein report that the use of a combination of alkyl fluorides^[9–12] and appropriate aryl Grignard reagents solves this problem, thus enabling the four-component coupling of alkyl fluorides, aryl Grignard reagents, and two 1,3-butadiene molecules that leads to the formation of 1,6-octadienes with alkyl and aryl groups at the 3- and 8-positions (Scheme 1d).^[13]

The reaction of *n*OctF (**1a**) and *o*TolMgBr (**2a**) with 1,3-butadiene was examined using 10 mol % of Group 10 metal salts in THF (Table 1). When NiBr₂(dme) was used, dimerization and coupling took place regio- and stereoselectively to give the *E*-configured four-component-coupling product **3aa** in 92 % yield (Table 1, entry 1). As a side product, 2-

Table 1: Four-component coupling reaction of 1,3-butadiene, *n*OctF, and *o*TolMgBr.

Entry	Cat. (mol %)	2a [equiv]	<i>T</i> [°C]	3aa [%] ^[a]
1	NiBr ₂ (dme) (10)	2.0	30	92
2	NiCl ₂ (PPh ₃) ₂ (10)	2.0	30	43
3	NiCl ₂ (dppf) (10)	2.0	30	8
4	PdCl ₂ (10)	2.0	30	4
5	PtCl ₂ (10)	2.0	30	n.d.
6	NiBr ₂ (dme) (10)	1.5	30	88
7	NiBr ₂ (dme) (5)	1.5	30	79
8	NiBr ₂ (dme) (5)	1.5	40	87 (86)

[a] Determined by GC (yields of isolated products given in parentheses). dme = 1,2-dimethoxyethane, dppf = 1,1'-bis(diphenylphosphino)ferrocene, *o*Tol = *ortho*-tolyl.

[*] Dr. T. Iwasaki, X. Min, A. Fukuoka, Prof. Dr. H. Kuniyasu, Prof. Dr. N. Kambe
Department of Applied Chemistry
Graduate School of Engineering, Osaka University
Suita, Osaka 565-0871 (Japan)
E-mail: iwasaki@chem.eng.osaka-u.ac.jp
kambe@chem.eng.osaka-u.ac.jp

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under
<http://dx.doi.org/10.1002/ange.201601126>.

octyltoluene was formed in only 4 % yield by the direct coupling of *n*OctF with *o*TolMgBr, but three-component-coupling products comprising one molecule each of 1,3-butadiene, **1a**, and **2a** were not detected at all.^[4,14] The use of PPh₃ and dppf affected the reaction, resulting in lower yields (entries 2 and 3), and Pd and Pt catalysts were found to be ineffective (entries 4 and 5). The amount of *o*TolMgBr could be reduced to 1.5 equiv without a substantial loss of efficiency (entry 6). The desired product was obtained in good yield (87 %) when 5 mol % of the Ni catalyst were used at 40 °C (entry 8). When an alkyl chloride, bromide, iodide, or mesylate was used instead of the alkyl fluoride, the desired product was obtained in 4, 64, 45, and 16 % yield, respectively.^[15] Under the same conditions, isoprene afforded a mixture of four regioisomers having two methyl groups at the different positions of the 1,6-octadiene skeleton, and the reaction of 1,3-pentadiene was sluggish. When alkyl Grignard reagents were employed instead of aryl Grignard reagents, the direct cross-coupling of the alkyl fluoride with the alkyl Grignard reagent predominated.^[9a]

Under the optimized reaction conditions (Table 1, entry 8), we investigated the scope and limitations of Grignard reagents (Table 2). When 2-substituted and even more sterically congested 2,6-disubstituted aryl Grignard reagents were employed, the coupling reaction proceeded smoothly to give the corresponding products **3** in excellent yields (entries 1–3). However, an *ortho*-methoxy group significantly affected the reaction (entry 4). The use of *p*-FC₆H₄MgBr (**2f**) resulted in the desired product in moderate yield (48 %), accompanied by the corresponding direct cross-coupling product, *n*OctAr, in 37 % yield. On the other hand, the introduction of an *ortho*-methyl group (**2g**) increased the yield to 77 % (entries 5 and 6). These results suggest that *ortho* substituents sterically suppress the nucleophilic attack of the Ni center towards the alkyl fluoride^[8,9a] (see below). An electron-donating methyl group at the *para* position led to an increased yield, whereas electron-withdrawing substituents somewhat reduced the yields (entries 6–9). The 2-methyl-1-naphthyl Grignard reagent **2k** gave **3ak** in 81 % yield (entry 10), whereas thienyl Grignard reagent **2l** resulted in a lower yield (entry 11).

As shown in Scheme 2, alkyl fluorides with various functional groups afforded the corresponding four-component-coupling products **3** in good to excellent yields. 11-

Table 2: Scope and limitations.^[a]

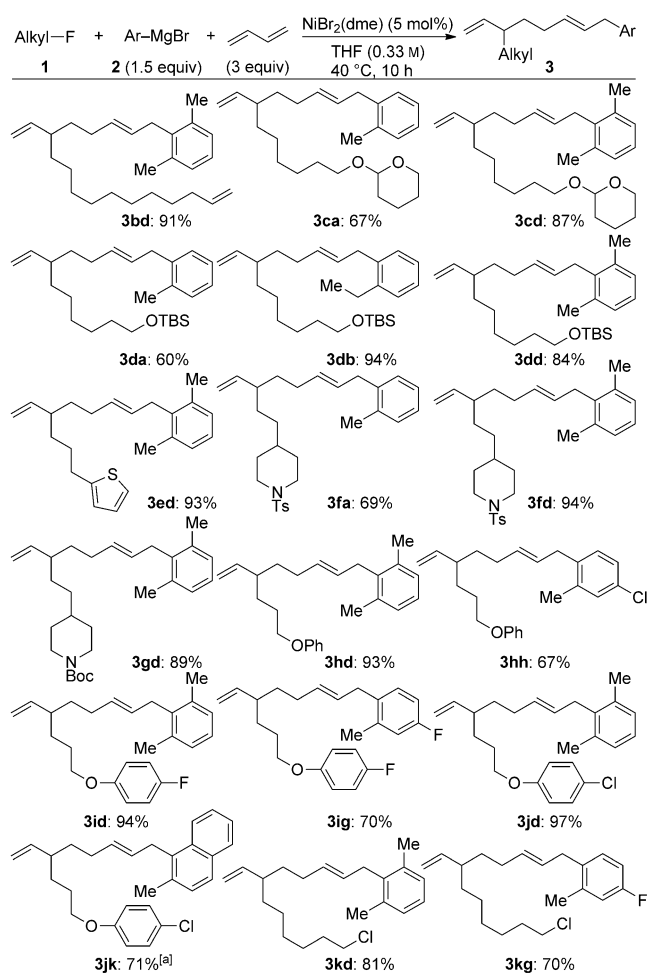
$n\text{Oct}-\text{F} + \text{Ar}-\text{MgBr} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \xrightarrow[\text{THF (0.33 M), 40 }^\circ\text{C, 10 h}]{\text{NiBr}_2(\text{dme}) \text{ (5 mol\%)}}$ $\textbf{1a} \quad \textbf{2 (1.5 equiv)} \quad \textbf{(3 equiv)} \quad \textbf{3}$					
Entry	ArMgBr	Yield [%]	Entry	ArMgBr	Yield [%]
1		89	7		66
2		85	8		96
3		90	9		67
4		n.d.	10 ^[c]		81
5 ^[b]		48	11		27
6		77			

[a] For the reaction conditions, see Table 1, entry 8. [b] With 10 mol % of the Ni catalyst at 30 °C for 24 h. 37 % of *n*OctAr was obtained. [c] At a 0.1 M concentration of **1a** in THF for 20 h.

Fluoro-1-undecene (**1b**) participated in the reaction to give **3bd** in 91 % yield without isomerization of the terminal double bond. Acid-sensitive tetrahydropyranyl and *tert*-butyldimethylsilyl (TBS) ethers as well as thiophene and *N*-tosyl and *N*-Boc piperidine were all tolerated. Furthermore, C(sp²)-F and C(sp²)-Cl bonds as well as C(sp³)-Cl bonds in the alkyl fluorides remained intact. In all cases, the desired product was formed exclusively, and no side products were formed except for small amounts of the direct cross-coupling products.

When 6-fluoro-1,1-diphenyl-1-hexene (**1l**) was employed in an attempt to examine the possibility of radical intermediates in the reaction, the corresponding product **3ld** was obtained in 93 % yield without any evidence for a 5-*exo* radical cyclization,^[16] suggesting that the alkylation process proceeds through an ionic pathway [Eq. (1)].

To gain insight into the mechanism of the present reaction, we conducted control experiments with NiBr₂(dme), 1.1 equiv of *n*OctF (**1a**), and 2 to 4 equiv of the Grignard reagent **2a** in the presence of an excess amount of 1,3-butadiene (Table 3). When 2 equiv of the Grignard reagent **2a** were used, the Ni^{II} species should be reduced to Ni⁰ and



Scheme 2. Nickel-catalyzed four-component couplings with various alkyl fluorides. [a] At a 0.1 M concentration of **1** for 20 h. Boc = *tert*-butoxycarbonyl, TBS = *tert*-butyldimethylsilyl, Ts = *para*-toluenesulfonyl.

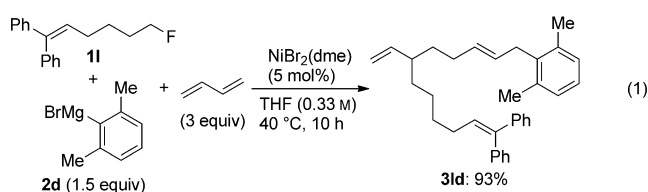
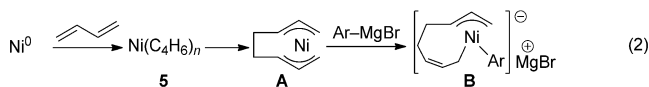


Table 3: Stoichiometric reactions of the Ni^{II} catalyst with **1a** and **2a**.

$n\text{Oct-F} + o\text{Tol-MgBr} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \xrightarrow[\text{THF, 40 }^\circ\text{C, 3 h}]{\text{NiBr}_2(\text{dme}) (0.5 \text{ mmol})}$			
Entry	<i>o</i> -TolMgBr	Conv. 1a [%]	3aa [%]
1	2 equiv	14	10
2	3 equiv	80	75
3	4 equiv	99	95

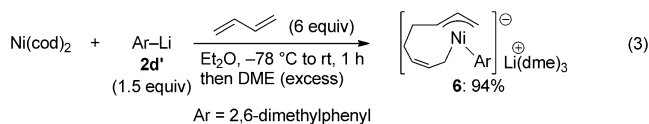
react with 1,3-butadiene to form π -complexes **5**, which results in the oxidative dimerization of 1,3-butadiene to give bis(π -allyl)nickel intermediate **A** [Eq. (2)]. When the mixture was



stirred at 40 °C for 3 h, only 14 % of **1a** were consumed, and **3aa** was formed in 10 % yield, suggesting that π -complexes **5**^[17] and bis(π -allyl)nickel intermediate **A** are inert towards alkyl fluorides (entry 1). When 3 equiv of **2a** were used, **3aa** was formed in 75 % yield, and a nearly quantitative yield of **3aa** was obtained by using 4 equiv of **2a** (entries 2 and 3). These results indicate that the present reaction is catalyzed by an anionic nickel complex **B** that is generated by the reaction of bis(π -allyl)nickel intermediate **A** with Grignard reagents [Eq. (2)].

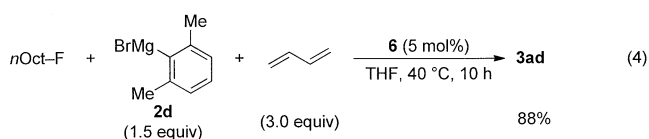
To confirm the formation of nickelate intermediate **B**, Ni(cod)₂ was treated with 5 equiv of 1,3-butadiene in [D₈]THF at room temperature, and the mixture was examined by NMR spectroscopy. The NMR spectrum showed signals corresponding to Ni(cod)₂ and free COD, accompanied by new broad signals at 4.7–6.5 ppm, along with the disappearance of the signals for free 1,3-butadiene.^[15] The broad resonances were assigned to π -complexes **5**, which are in rapid equilibrium with free 1,3-butadiene.^[15] The addition of 2 equiv of Grignard reagent **2d** to the reaction mixture led to the generation of a new species with an aryl group and a dimerized 1,3-butadiene moiety in a 1:1 ratio. This could be nickelate **B**, which is formed via bis(π -allyl)nickel **A**, which in turn is generated transiently or exists at a low concentration in equilibrium with **5** and/or **B** [Eq. (2)].^[15, 17c, 18]

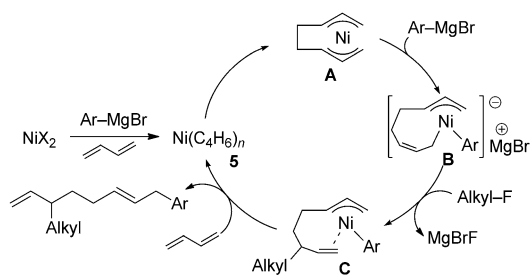
Nickelate **6** was isolated as an orange semisolid in 94 % yield using 2,6-dimethylphenyllithium **2d'** [Eq. (3)], and



shows resonances corresponding to 2,6-dimethylphenyl, σ -allyl, and π -allyl groups in its NMR spectra.^[15] When isolated nickelate **6** was employed as the catalyst in the reaction of *n*OctF with Grignard reagent **2d**, the corresponding product **3ad** was obtained in 88 % yield [Eq. (4)], strongly supporting the intermediacy of **B**.

Based on these results, a plausible reaction pathway is proposed in Scheme 3. Reduction of the Ni^{II} salt by the aryl Grignard reagent gives a Ni⁰ species, which then participates





Scheme 3. Plausible reaction mechanism.

in the oxidative dimerization of 1,3-butadiene to give bis(π -allyl)nickel intermediate **A** via π -complex **5**.^[17] Complex **A** readily reacts with the aryl Grignard reagent to form an anionic complex **B**,^[18] which is inert towards the further insertion of 1,3-dienes but possesses enhanced nucleophilicity. Although complex **B** has four potent nucleophilic centers, namely the α - and γ -carbon atoms of the σ -allyl group, the *ipso* carbon atom of the aryl group, and the Ni center,^[19] alkyl fluorides react selectively at the γ -carbon atom of the σ -allyl group in **B** to give intermediate **C** by an S_N2 mechanism in a process that is probably assisted by the coordination of MgX cations to the eliminating F anion. Substituent(s) at the *ortho* position(s) of the aryl group block the approach of alkyl halides towards the Ni center and the *ipso* carbon atom. The observed perfect γ -regioselectivity of the allylation can be explained by the facile transition from σ -coordination to π -coordination of the Ni species upon going from **B** to **C**. Subsequent reductive elimination gives four-component coupling products with regeneration of the Ni^0 species.

Telomerization and related transformations (Scheme 1 a and b) are useful for constructing functionalized C8 frameworks, but often suffer from side reactions, including 1) the direct functionalization of the 1,3-diene without dimerization^[3c,4,14] and 2) oligomerization of the 1,3-dienes,^[2d,e] and from poor product selectivities with respect to 3) the regioselectivity of C–C bond formation with nucleophiles and/or electrophiles^[2a–c] and 4) the stereochemistry of the newly formed internal C–C double bonds.^[4a,c,5,6] In contrast, the present reaction resulted in perfect selectivities and appears to proceed through a unique mechanism that involves an anionic complex **B** as the active catalytic species.

In conclusion, we have disclosed herein that a nickel complex catalyzes the dimerization and alkylarylation of 1,3-butadiene with alkyl fluorides and aryl Grignard reagents to give 3-alkyl-8-aryl-1,6-octadienes. The present catalytic reaction tolerates a wide variety of functional groups, and $C(sp^3)$ –F bonds were cleaved efficiently and selectively.^[11] As a catalytically active species towards alkyl fluorides, anionic nickel complexes play an important role in the formation of C–C bonds by C–F bond cleavage.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (A) (25248025), a JSPS Japanese–

German Graduate Externship from the JSPS, and a Grant-in-Aid for Scientific Research on Innovative Area “Molecular Activation Directed toward Straightforward Synthesis” (2204) from MEXT. T.I. thanks the UBE Foundation and the Sumitomo Foundation.

Keywords: alkylation · dimerization · multicomponent reactions · nickel · regioselectivity

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 5550–5554
Angew. Chem. **2016**, *128*, 5640–5644

- [1] a) G. H. Posner, *Chem. Rev.* **1986**, *86*, 831; b) R. W. Armstrong, A. P. Combs, P. A. Tempest, S. D. Brown, T. A. Keating, *Acc. Chem. Res.* **1996**, *29*, 123; c) H. Bienaymé, C. Hulme, G. Odon, P. Schmitt, *Chem. Eur. J.* **2000**, *6*, 3321.
- [2] a) E. J. Smutny, *J. Am. Chem. Soc.* **1967**, *89*, 6793; b) S. Takahashi, T. Shibano, N. Hagihara, *Tetrahedron Lett.* **1967**, *8*, 2451; the use of active methylene or methyl compounds as carbon nucleophiles was also reported; see: c) T. Mitsuyasu, M. Hara, J. Tsuji, *Chem. Commun.* **1971**, 345; d) G. Hata, K. Takahashi, A. Miyake, *J. Org. Chem.* **1971**, *36*, 2116; e) R. Baker, D. E. Halliday, T. M. Smith, *J. Organomet. Chem.* **1972**, *35*, C61; for reviews, see: f) A. Behr, M. Becker, T. Beckmann, L. Johnen, J. Leschinski, S. Reyer, *Angew. Chem. Int. Ed.* **2009**, *48*, 3598; *Angew. Chem.* **2009**, *121*, 3652; g) R. Baker, *Chem. Rev.* **1973**, *73*, 487; h) W. Keim, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235; *Angew. Chem.* **1990**, *102*, 251; i) S. M. Sieburth, N. T. Cunard, *Tetrahedron* **1996**, *52*, 6251; j) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49.
- [3] a) W. E. Billups, W. E. Walker, T. C. Shields, *Chem. Commun.* **1971**, 1067; b) J. Tsuji, Y. Mori, M. Hara, *Tetrahedron* **1972**, *28*, 3721; for a review, see: c) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510; *Angew. Chem.* **2011**, *123*, 8662.
- [4] For the use of aldehydes, see: a) M. Kimura, S. Matsuo, K. Shibata, Y. Tamaru, *Angew. Chem. Int. Ed.* **1999**, *38*, 3386; *Angew. Chem.* **1999**, *111*, 3586; ketones: b) M. Kimura, A. Ezoe, M. Mori, Y. Tamaru, *J. Am. Chem. Soc.* **2005**, *127*, 201; imines: c) K. Kojima, M. Kimura, Y. Tamaru, *Chem. Commun.* **2005**, 4717; d) M. Kimura, Y. Tatsuyama, K. Kojima, Y. Tamaru, *Org. Lett.* **2007**, *9*, 1871.
- [5] J. Terao, A. Oda, A. Ikumi, A. Nakamura, H. Kuniyasu, N. Kambe, *Angew. Chem. Int. Ed.* **2003**, *42*, 3412; *Angew. Chem.* **2003**, *115*, 3534.
- [6] J. Terao, A. Oda, N. Kambe, *Org. Lett.* **2004**, *6*, 3341.
- [7] a) D. J. Cárdenas, *Angew. Chem. Int. Ed.* **2003**, *42*, 384; *Angew. Chem.* **2003**, *115*, 398; b) M. R. Netherton, G. C. Fu, *Adv. Synth. Catal.* **2004**, *346*, 1525; c) A. C. Frisch, M. Beller, *Angew. Chem. Int. Ed.* **2005**, *44*, 674; *Angew. Chem.* **2005**, *117*, 680; d) J. Terao, N. Kambe, *Acc. Chem. Res.* **2008**, *41*, 1545; e) N. Kambe, T. Iwasaki, J. Terao, *Chem. Soc. Rev.* **2011**, *40*, 4937; f) X. L. Hu, *Chem. Sci.* **2011**, *2*, 1867.
- [8] For nickel-catalyzed cross-coupling reactions using 1,3-butadiene as an additive, see: a) J. Terao, H. Watanabe, A. Ikumi, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* **2002**, *124*, 4222; b) T. Iwasaki, K. Higashikawa, V. P. Reddy, W. W. S. Ho, Y. Fujimoto, K. Fukase, J. Terao, H. Kuniyasu, N. Kambe, *Chem. Eur. J.* **2013**, *19*, 2956; c) A. Ghaderi, T. Iwasaki, A. Fukuoka, J. Terao, N. Kambe, *Chem. Eur. J.* **2013**, *19*, 2951.
- [9] For the use of alkyl fluorides in cross-coupling reactions, see: a) J. Terao, A. Ikumi, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* **2003**, *125*, 5646; b) J. Terao, H. Todo, H. Watanabe, A. Ikumi, N. Kambe, *Angew. Chem. Int. Ed.* **2004**, *43*, 6180; *Angew. Chem.* **2004**, *116*, 6306; c) J. Terao, H. Todo, S. A. Begum, H. Kuniyasu, N. Kambe, *Angew. Chem. Int. Ed.* **2007**, *46*, 2086; *Angew. Chem.*

- 2007, 119, 2132; d) T. Iwasaki, H. Takagawa, S. P. Singh, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* **2013**, 135, 9604; e) T. Iwasaki, R. Imanishi, R. Shimizu, H. Kuniyasu, J. Terao, N. Kambe, *J. Org. Chem.* **2014**, 79, 8522.
- [10] For the copper-catalyzed 1,2-hydroalkylation of 1,3-dienes with alkyl fluorides, see: T. Iwasaki, R. Shimizu, R. Imanishi, H. Kuniyasu, N. Kambe, *Angew. Chem. Int. Ed.* **2015**, 54, 9347; *Angew. Chem.* **2015**, 127, 9479.
- [11] For representative reviews on C–F bond cleavage in organic synthesis, see: a) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, 94, 373; b) T. Braun, R. N. Perutz, *Chem. Commun.* **2002**, 2749; c) H. Torrents, *Coord. Chem. Rev.* **2005**, 249, 1957; d) J. Terao, H. Todo, H. Watabe, A. Ikumi, Y. Shinohara, N. Kambe, *Pure Appl. Chem.* **2008**, 80, 941; e) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, 109, 2119.
- [12] For cross-coupling reactions of alkyl fluorides, see: a) T. Ooi, D. Uraguchi, N. Kagoshima, K. Maruoka, *Tetrahedron Lett.* **1997**, 38, 5679; b) K. Hirano, K. Fujita, H. Yorimitsu, H. Shinokubo, K. Oshima, *Tetrahedron Lett.* **2004**, 45, 2555; c) T. Hatakeyama, S. Ito, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2005**, 127, 14192; d) J. Terao, S. A. Begum, Y. Shinohara, M. Tomita, Y. Naitoh, N. Kambe, *Chem. Commun.* **2007**, 855; e) M. Sai, H. Someya, H. Yorimitsu, K. Oshima, *Org. Lett.* **2008**, 10, 2545; f) Z. Mo, Q. Zhang, L. Deng, *Organometallics* **2012**, 31, 6518.
- [13] For recent reviews on transformations of 1,6-dienes, see: a) I. D. G. Watson, F. D. Toste, *Chem. Sci.* **2012**, 3, 2899; b) Y. Yamamoto, *Chem. Rev.* **2012**, 112, 4736; c) C. Aïssa, *Synlett* **2014**, 2379.
- [14] For reviews on the reaction of carbonyl compounds, 1,3-butadiene, and organometallic reagents in a 1:1:1 ratio, see: a) Y. Tamaru, *J. Organomet. Chem.* **1999**, 576, 215; b) S.-i. Ikeda, *Angew. Chem. Int. Ed.* **2003**, 42, 5120; *Angew. Chem.* **2003**, 115, 5276; c) J. Montgomery, *Angew. Chem. Int. Ed.* **2004**, 43, 3890; *Angew. Chem.* **2004**, 116, 3980; d) M.-Y. Ngai, J.-R. Kong, M. J. Krische, *J. Org. Chem.* **2007**, 72, 1063; e) J. M. Ketcham, I. Shin, T. P. Montgomery, M. J. Krische, *Angew. Chem. Int. Ed.* **2014**, 53, 9142; *Angew. Chem.* **2014**, 126, 9294.
- [15] See the Supporting Information for details.
- [16] The rate constant for the cyclization has been determined to be $k = 4.0 \times 10^7 \text{ s}^{-1}$ at 25 °C; see: M. Newcomb, S.-Y. Choi, J. H. Horner, *J. Org. Chem.* **1999**, 64, 1225.
- [17] a) G. Wilke, B. Bogdanović, P. Borner, H. Breil, P. Hardt, P. Heimbach, G. Herrmann, H.-J. Kaminsky, W. Keim, M. Kröner, H. Müller, E. W. Müller, W. Oberkirch, J. Schneider, J. Stedeffeder, K. Tanaka, K. Weyer, *Angew. Chem. Int. Ed. Engl.* **1963**, 2, 105; *Angew. Chem.* **1963**, 75, 10; b) B. Barnett, B. Büssemeier, P. Heimbach, P. W. Jolly, C. Krüger, I. Tkatchenko, G. Wilke, *Tetrahedron Lett.* **1972**, 13, 1457; c) R. Benn, B. Büssemeier, S. Holle, P. W. Jolly, R. Mynott, I. Tkatchenko, G. Wilke, *J. Organomet. Chem.* **1985**, 279, 63.
- [18] a) S. Holle, P. W. Jolly, R. Mynott, R. Salz, *Z. Naturforsch. B* **1982**, 37, 675; b) K. Jonas, C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1980**, 19, 520; *Angew. Chem.* **1980**, 92, 513.
- [19] a) J. Terao, Y. Naitoh, H. Kuniyasu, N. Kambe, *Chem. Commun.* **2007**, 825; b) T. Iwasaki, A. Tsumura, T. Omori, H. Kuniyasu, J. Terao, N. Kambe, *Chem. Lett.* **2011**, 40, 1024.

Received: January 31, 2016

Published online: March 3, 2016