Multicomponent Reactions

International Edition: DOI: 10.1002/anie.201601126
German Edition: DOI: 10.1002/ange.201601126

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

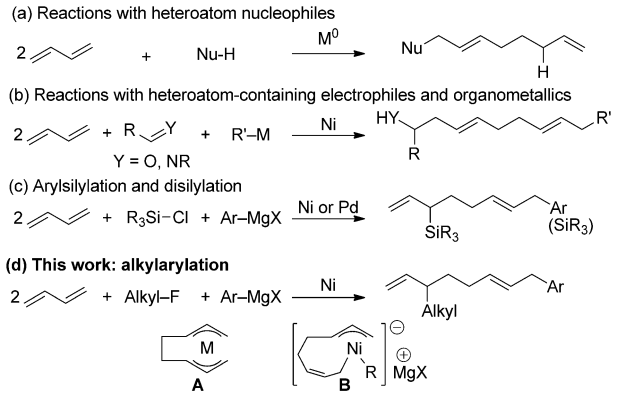
Takanori Iwasaki, Xin Min, Asuka Fukuoka, Hitoshi Kuniyasu, and Nobuaki Kambe**

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 1 a).[2] When CO or CO_2 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 1 b).[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]

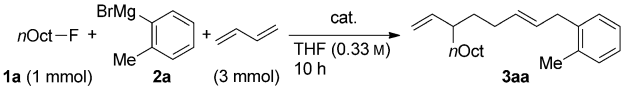
We previously reported on the dimerization and arylsilylation[5] or disilylation[6] of 1,3-butadiene with chlorosilanes as the electrophile in the presence of a Ni or Pd catalyst, respectively (Scheme 1 c). This reaction is promoted by Grignard reagents, which enable the formation of an anionic nickel 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 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 1 d).[13]



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

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 $NiBr_2$(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]	*T* [°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.

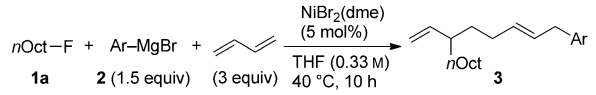
[*] Dr. T. Iwasaki, X. Min, A. Fukuoka, Prof. Dr. H. Kuniyasu, Prof. Dr. N. Kambe
Department of Applied Chemistry
Graduate School of Engineering, Osaka University
Suita, Osaka 565-0871 (Japan)
E-mail: iwasaki@chem.eng.osaka-u.ac.jp
kambe@chem.eng.osaka-u.ac.jp

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

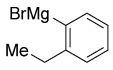
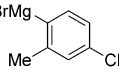
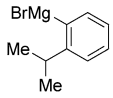
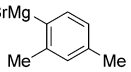
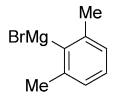
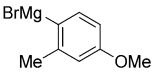
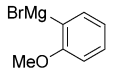
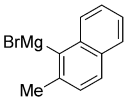
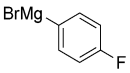
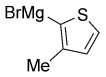
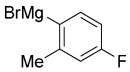
 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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 PPh_3 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]

Table 2: Scope and limitations.[a]



1a | 2 (1.5 equiv) | (3 equiv) | 3

Entry	ArMgBr	Yield [%]	Entry	ArMgBr	Yield [%]
1	 **2b**	89	7	 **2h**	66
2	 **2c**	85	8	 **2i**	96
3	 **2d**	90	9	 **2j**	67
4	 **2e**	n.d.	10[c]	 **2k**	81
5[b]	 **2f**	48	11	 **2l**	27
6	 **2g**	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.

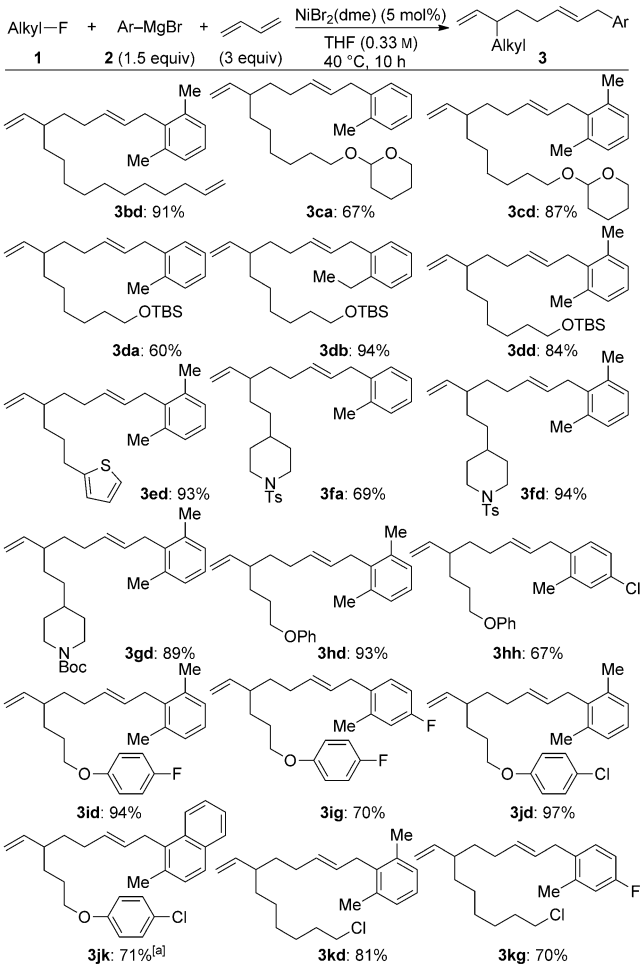
Under the optimized reaction conditions (Table 1, entry 8), we investigated the scope and limitations of Grignard reagents (Table 2). When 2-substituted and even more sterically congested 2,6-disubstituted aryl Grignard reagents were employed, the coupling reaction proceeded smoothly to give the corresponding products **3** in excellent yields (entries 1–3). However, an *ortho*-methoxy group significantly affected the reaction (entry 4). The use of *p*-FC_6H_4MgBr (**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-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, $C(sp^2)$–F and $C(sp^2)$–Cl bonds as well as $C(sp^3)$–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.

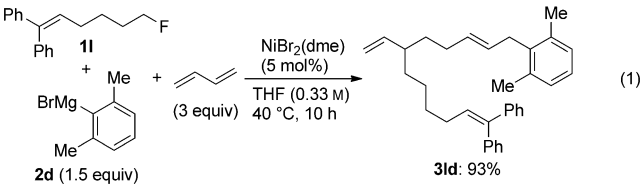
When 6-fluoro-1,1-diphenyl-1-hexene (**1l**) was employed in an attempt to examine the possibility of radical intermediates in the reaction, the corresponding product **3ld** was obtained in 93% yield without any evidence for a 5-*exo* radical cyclization,[16] suggesting that the alkylation process proceeds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

To gain insight into the mechanism of the present reaction, we conducted control experiments with $NiBr_2$(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 Ni^0 and

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

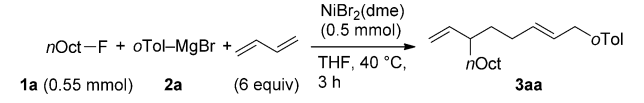


Scheme 2. Nickel-catalyzed four-component couplings with various alkyl fluorides. [a] At a 0.1 M concentration of **1** for 20 h. Boc = *tert*-butoxycarbonyl, TBS = *tert*-butyldimethylsilyl, Ts = *para*-toluenesulfonyl.



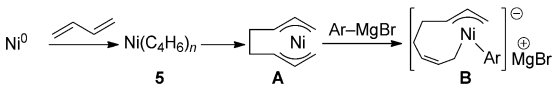
(1)

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



Entry	*o*-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

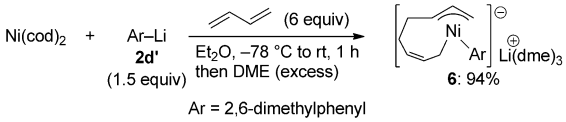


(2)

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 $[D_8]$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]

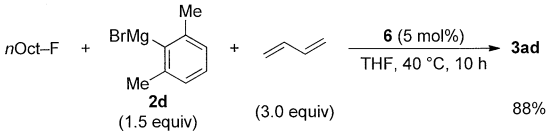
Nickelate **6** was isolated as an orange semisolid in 94 % yield using 2,6-dimethylphenyllithium **2d′** [Eq. (3)], and



(3)

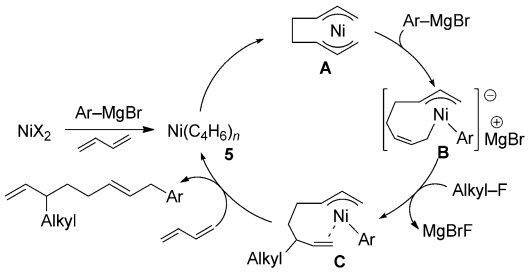
shows resonances corresponding to 2,6-dimethylphenyl, σ-allyl, and π-allyl groups in its NMR spectra.[15] When isolated nickelate **6** was employed as the catalyst in the reaction of *n*OctF with Grignard reagent **2d**, the corresponding product **3ad** was obtained in 88 % yield [Eq. (4)], strongly 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 Ni^0 species, which then participates



(4)

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



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. Oddon, 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.*

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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. Torrens, *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 $k = 4.0 \times 10^7\ s^{-1}$ at 25 °C; see: M. Newcomb, S.-Y. Choi, J. H. Horner, *J. Org. Chem.* **1999**, *64*, 1225.

[17] a) G. Wilke, B. Bogdanovič, 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. Stedefeder, 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

 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim