Organic LETTERS

Letter

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$B(C_6F_5)_3$-Catalyzed Michael Reactions: Aromatic C−H as Nucleophiles

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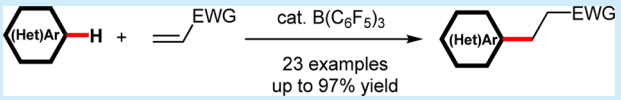
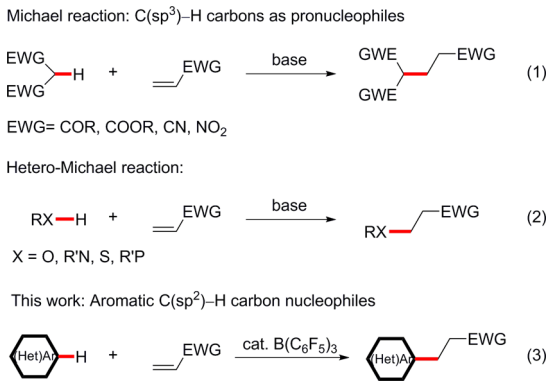
Supporting Information

ABSTRACT: The Michael reaction is a widely used reaction for the C−C coupling of electron-poor olefins and $C(sp^3)$−H pronucleophiles. Herein we report the Michael reaction between alkenes and aromatic as well as heteroaromatic compounds as aromatic $C(sp^2)$−H nucleophiles under mild conditions. The reaction is catalyzed by readily available Lewis acidic $B(C_6F_5)_3$ and proceeds with high regioselectivity for a wide substrate scope.



The Michael reaction, namely the addition of an enolate to an activated alkene such as an α,β-unsaturated carbonyl compound, is one of the most efficient and effective routes to the formation of C−C bonds (Scheme 1, eq 1).[1] Since its discovery by Arthur Michael in the late 1880s, the Michael reaction has been extensively studied, and numerous variants of this reaction have been developed.[2] The hetero-Michael addition including the *oxa-*,[3] *aza-*,[4] *thia-*,[5] and *phospha*-Michael reactions[6] is the extension of this concept to heterocentered anions (Scheme 1, eq 2). These reactions have been widely implemented in organic synthesis and in material science.[7] In addition, the Michael reaction has been utilized in polymer synthesis for biomedical applications such as gene transfection,[8] cell scaffolds,[9] tissue replacements,[10] and biomaterials for pH-sensitive drug delivery.[11] Owing to the perfect atom economy, the benefit from mild reaction conditions and high functional group tolerance, the Michael and the hetero-Michael reaction have become a comprehensive toolbox to prepare specific, highly functionalized products.[12] Over the past 130 years the nucleophiles employed in the Michael reaction were mainly based on the following: (1) Substrates containing $C(sp^3)$−H bonds with electron-withdrawing groups, such as acyl and cyano, which increase the acidity of the methylene hydrogens. This facilitates the formation of the respective carbanion by deprotonation with a suitable base. (2) Substrates with a hetero−H such as ROH, R_2NH, RSH, and R_2PH. Notably, only a few examples were developed using more challenging aromatic $C(sp^2)$−H as the nucleophile.[13] Franzén and Bah reported a Michael reaction using *N,N*-dimethylaniline and highly activated ethyl-4-oxo-2-butenoate as Michael acceptors in the presence of a carbocation at room temperature.[14] However, the substrate scope of this catalytic system is limited. More recently, a cationic anti-Bredt di(amino)carbene gold(I) complex catalyzed hydroarylation of enones with *N,N*-dialkylanilines at 120 or 135 °C was reported by Bertrand and co-workers.[15]

Scheme 1. Michael Reaction Utilizing Different (Pro-)nucleophiles



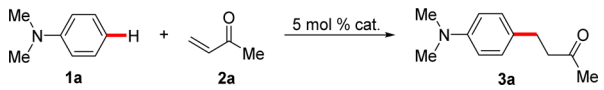
Tris(pentafluorophenyl)-borane based catalytic systems have been successfully employed in various important organic transformations including hydrogenation reactions,[16] hydrosilylation[17] of unsaturated organic functions, such as C=O and C=C bonds, dehydrogenative coupling of alcohols,[18] thiols,[19] or amines,[20] dehydrogenative oxidation,[21] polymerizations,[22] and other transformations.[23] In addition, $B(C_6F_5)_3$ also plays a significant role as a component of frustrated Lewis pairs.[24] Only a few examples have been demonstrated for $B(C_6F_5)_3$ catalyzed C−C bond formation.[25] In general, as a strong Lewis acid, $B(C_6F_5)_3$ can activate the carbonyl group via coordination to one of the oxygen lone pairs. Accordingly, our design is to employ $B(C_6F_5)_3$ as a Lewis acid activating the α,β-unsaturated carbonyl compound to facilitate the addition of electron-rich aromatics. Herein, we report the first $B(C_6F_5)_3$-catalyzed Michael reaction with aromatic and heteroaromatic $C(sp^2)$−H as the nucleophiles (Scheme 1, eq 3).

The hydroarylation of methyl vinyl ketone (**2a**) with *N,N*-dimethylaniline (**1a**) was chosen as a test reaction. Notably, no product was detected in the absence of $B(C_6F_5)_3$ (Table 1, entry 1). However, in the presence of 5 mol % $B(C_6F_5)_3$ as the catalyst and $CHCl_3$ as the solvent at 80 °C, the desired product **3a** was obtained in 91% yield after a reaction time of 24 h (entry 2). A lower reaction temperature resulted in a decrease in yield, affording a yield of 52% for **3a** (entry 3). $CHCl_3$ sometimes contains traces of HCl. Thus, mesitylene was used

Received: March 25, 2017

DOI: 10.1021/acs.orglett.7b00720
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Hydroarylation of Methyl Vinyl Ketone (2a) with *N,N*-Dimethylaniline (1a)[a]



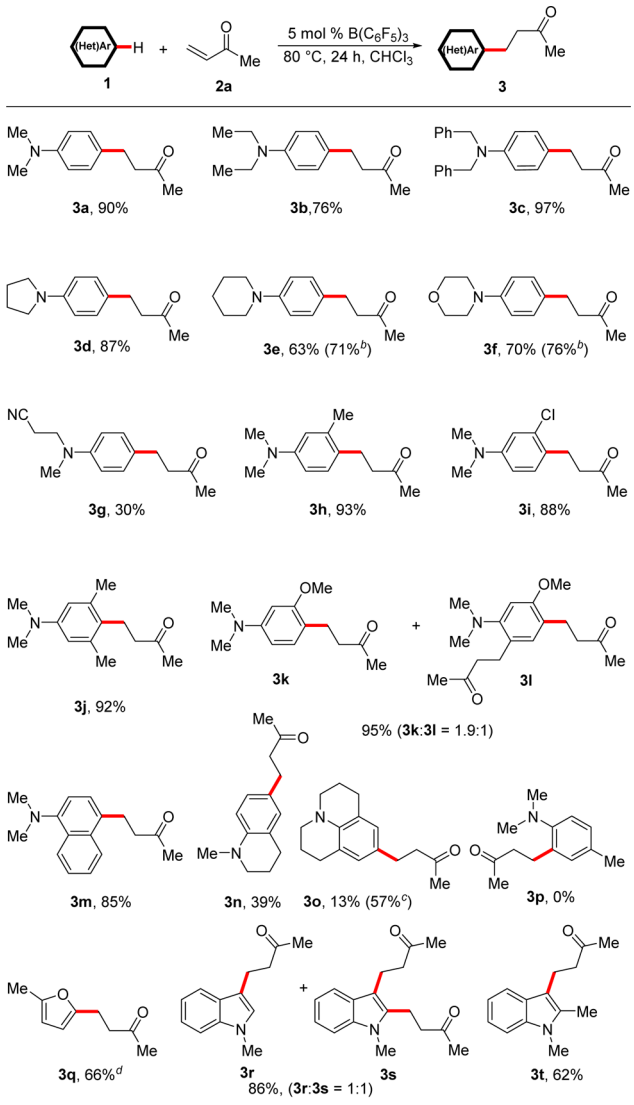
entry	catalyst	temp/°C	solvent	yield (%)[b]
1	–	80	$CHCl_3$	0
2	$B(C_6F_6)_3$	80	$CHCl_3$	91
3	$B(C_6F_6)_3$	40	$CHCl_3$	52
4	$B(C_6F_6)_3$	80	mesitylene	82[c]
5	$Zn(OAc)_2$	80	$CHCl_3$	0
6	$ZnCl_2$	80	$CHCl_3$	19
7	$FeCl_3$	80	$CHCl_3$	27
8	$TrBF_4$	80	$CHCl_3$	0
9	$PhCO_2H$	80	$CHCl_3$	0
10	$B(C_6F_6)_3$	80	$CHCl_3$	76[d]

[a]Standard reaction conditions: **1a** (2.0 mmol), **2a** (4.0 mmol), cat. (0.1 mmol), solvent (2.0 mL), 40 or 80 °C for 24 h. [b]Determined by ^{1}H NMR with mesitylene as internal standard. [c]Isolated yield. [d]2.5 mol % $B(C_6F_6)_3$ was used.

as a solvent to study the influence of a trace amount HCl. However, the yield only slightly decreased to 82% (entry 2 vs 4). Notably, in the presence of other common transition metal Lewis acids such as $Zn(OAc)_2$, $ZnCl_2$, and $FeCl_3$ as catalysts, no product was detected or significantly lower yields were obtained (entries 5–7). In the presence of $TrBF_4$ (Triphenylcarbenium tetrafluoroborate) as Lewis acidic organocatalyst or benzoic acid as a Brønsted acidic catalyst, the formation of **3a** was also not observed (entries 8 and 9). Lowering the catalyst loading resulted in a 76% yield of the desired product (entry 10).

With the optimized conditions in hand, we focused our attention on the substrate scope. Thus, a range of electron-rich aromatic substrates as well as aromatic heterocycles were converted under the optimized conditions (Scheme 2). Overall, all of the substrates were usually readily converted into the corresponding Michael reaction products **3a–3t** with high regioselectivity, and good to excellent isolated yields. For example, high yields were obtained when *N,N*-diethylaniline (**1b**) and *N,N*-dibenzylaniline (**1c**) were coupled with methyl vinyl ketone to give **3b** and **3c**, respectively. Aniline derivatives with cyclic moieties could be smoothly transformed into the desired products **3d** and **3e** with good yields. Moreover, 4-phenylmorpholine (**1f**) reacted well with **2a** and gave the corresponding *para*-substituted product **3f** in 70% yield. Increasing the reaction temperature from 80 to 100 °C led to a slightly improved yield of 76%. Importantly, in the case of substrate **1g** which contains a valuable cyano group, this functional group remained untouched under the reaction conditions. Furthermore, when we investigated the *N,N*-dimethylanilines **1h–1m** bearing either electron-donating or -withdrawing groups on the phenyl ring, the corresponding *β*-(aryl)ketones **3h–3m** were isolated in excellent yields (88%–93%) and regioselectivities. 3-Methoxy-*N,N*-dimethylaniline (**1k**) gave mixtures of mono- and dialkylated products in 95% overall yield. The reaction of *N,N*-dimethyl-1-naphthylamine (**1m**) gave the C4-substituted product **3m** in 85% yield under the standard reaction conditions. A low yield was isolated when 1-methyl-1,2,3,4-tetrahydroquinoline (**1n**) was employed as the substrate. The reaction of julolidine (**1o**) with **2a** gave the corresponding alkylated product **3o** in 13% yield. The yield

Scheme 2. Scope for the Conversion of Electron-Rich Aromatic and Heteroaromatic Substrates 1 with Methyl Vinyl Ketone (2a)[a]



[a]Standard reaction conditions: **1** (2.0 mmol), **2a** (4.0 mmol), $B(C_6F_5)_3$ (0.1 mmol), $CHCl_3$ (2.0 mL), 80 °C for 24 h, unless otherwise noted. Isolated yields are shown. [b]100 °C. [c]The reaction was carried out in mesitylene (2.0 mL) at 130 °C. [d]The reaction was carried out at room temperature.

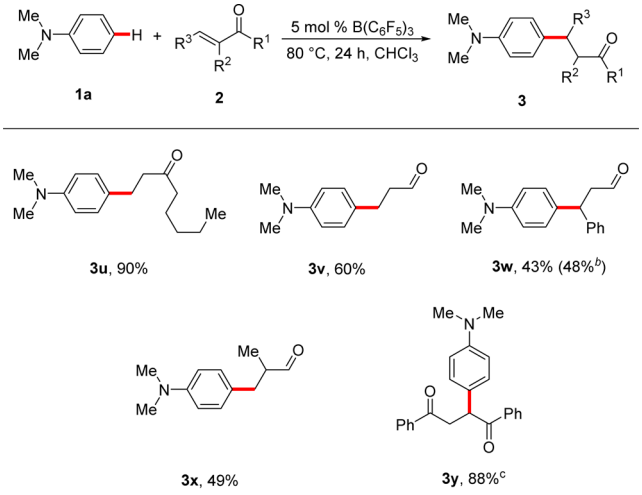
was improved to 57% in mesitylene as the solvent at a higher reaction temperature of 130 °C.

Notably, if the *para*-position was blocked, no *ortho*-substitution was observed, e.g., when *N,N*-dimethyl-*p*-toluidine (**1p**) was used as a substrate. The five-membered aromatic heterocycle 2-methylfuran (**1q**) proved to be a suitable substrate, and the corresponding product **3q** was obtained in 57% yield. Similarly, 1-methylindole (**1r**) underwent the reaction to generate a 1:1 mixture of mono- and dialkylated products in 86% overall yield, while 1,2-dimethyl-indole (**1t**) afforded **3t** in 62% yield.

In addition to further illustrate the scope of this reaction with respect to the Michael acceptor, several *α,β*-unsaturated carbonyl compounds **2** were converted with *N,N*-dimethylaniline (**1a**) (Scheme 3). The reaction of oct-1-en-3-one (**2b**) with

DOI: 10.1021/acs.orglett.7b00720
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 3. Substrate Scope of Various α,β-Unsaturated Carbonyl Compounds[a]

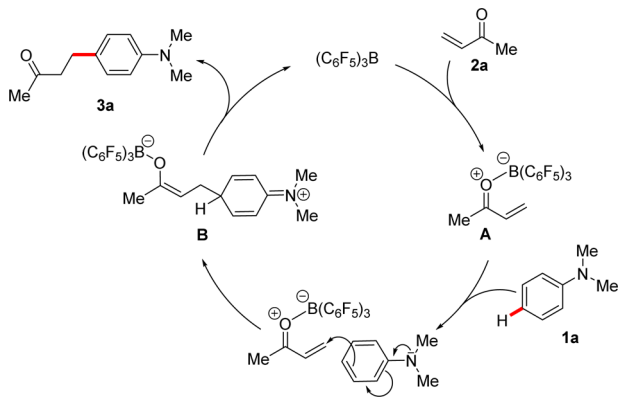


[a]Standard reaction conditions: **1a** (2.0 mmol), **2** (4.0 mmol), $B(C_6F_5)_3$ (0.1 mmol), $CHCl_3$ (2.0 mL), 80 °C for 24 h, unless otherwise noted. Isolated yields are shown. [b]The reaction was carried out in mesitylene (2.0 mL) at 130 °C, **1a** (4.0 mmol) and cinnamaldehyde (**2d**, 2.0 mmol). [c]**1a** (4.0 mmol) and (*E*)-1,4-diphenylbut-2-ene-1,4-dione (**2f**, 2.0 mmol).

1a led to the desired product **3u** in 90% yield. Notably, the conversion of α,β-unsaturated aldehydes such as acrylaldehyde (**2c**), cinnamaldehyde (**2d**), and methacrylaldehyde (**2e**) gave the desired products **3v**–**3w** in moderate yields between 43% and 60%. In contrast, the reaction of (*E*)-1,4-diphenylbut-2-ene-1,4-dione (**2f**) with *N*,*N*-dimethylaniline (**1a**) gave the corresponding adduct **3y** in 88% yield.

A putative reaction mechanism for the present $B(C_6F_5)_3$-catalyzed Michael reactions is depicted in Scheme 4. The initial

Scheme 4. Putative Mechanism for $B(C_6F_5)_3$-Catalyzed Michael Reaction



step of the reaction is probably the Lewis acidic activation of methyl vinyl ketone (**2a**) by $B(C_6F_5)_3$. The *in situ* generated electrophilic species **A** reacts with *N*,*N*-dimethylaniline (**1a**) in the *para* position to form intermediate **B**. Subsequent rearomatization and protonation of the enolate, followed by keto–enol tautomerization, led to the formation of product **3a** and regeneration of $B(C_6F_5)_3$.

In summary, we have developed the first $B(C_6F_5)_3$-catalyzed Michael addition reaction with both aromatic and heteroaromatic $C(sp^2)$–H as the nucleophiles and various α,β-unsaturated carbonyl compounds as electrophiles. The reaction proceeds for a wide range of substrates with high regioselectivity, and the desired products were usually obtained in good to excellent isolated yields. This $B(C_6F_5)_3$-catalyzed transformation complements the scope of Michael donors to a wide range of $C(sp^2)$–H nucleophiles. Studies on the mechanism of this reaction as well as other $B(C_6F_5)_3$-catalyzed transformations will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00720.

Experimental details, characterization data of all compounds, and copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We wish to thank Prof. M. Beller from the Leibniz Institute for Catalysis for his support and advice.

■ REFERENCES

(1) (a) Michael, A. *J. Prakt. Chem.* **1887**, *35*, 349–356. (b) Tokoroyama, T. *Eur. J. Org. Chem.* **2010**, 2009–2016.

(2) (a) Mather, B. D.; Viswanathan, K.; Miller, K. M.; Long, T. E. *Prog. Polym. Sci.* **2006**, *31*, 487–531. (b) Enders, D.; Lüttgen, K.; Narine, A. *Synthesis* **2007**, 959–980. (c) Vicario, J.; Badía, D.; Carrillo, L. *Synthesis* **2007**, 2065–2092. (d) Mukherjee, S.; Yang, J. W.; Hoffmann, S.; List, B. *Chem. Rev.* **2007**, *107*, 5471–5569. (e) Christoffers, J.; Scharl, H. *Eur. J. Org. Chem.* **2002**, 1505–1508. (f) Christoffers, J.; Baro, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1688–1690. (g) Christoffers, J.; Koripelly, G.; Rosiak, A.; Rössle, M. *Synthesis* **2007**, 1279–1300. (h) Rosiak, A.; Hoenke, C.; Christoffers, J. *Eur. J. Org. Chem.* **2007**, 4376–4382. (i) Asthalter, T.; Rajagopalan, S.; Kauf, T.; Rabe, V.; Christoffers, J. *J. Phys. Chem. A* **2008**, *112*, 11514–11518.

(3) (a) Nising, C. F.; Brase, S. *Chem. Soc. Rev.* **2008**, *37*, 1218–1228. (b) Nising, C. F.; Brase, S. *Chem. Soc. Rev.* **2012**, *41*, 988–999. (c) Stewart, I. C.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 8696–8697. (d) Enders, D.; Haertwig, A.; Raabe, G.; Runsink, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2388–2390.

(4) (a) Wabnitz, T. C.; Yu, J. Q.; Spencer, J. B. *Chem.–Eur. J.* **2004**, *10*, 484–493. (b) Sanchez-Rosello, M.; Acena, J. L.; Simon-Fuentes, A.; del Pozo, C. *Chem. Soc. Rev.* **2014**, *43*, 7430–7453.

(5) (a) Krenske, E. H.; Petter, R. C.; Zhu, Z.; Houk, K. N. *J. Org. Chem.* **2011**, *76*, 5074–5081. (b) Avonto, C.; Taglialatela-Scafati, O.; Pollastro, F.; Minassi, A.; Di Marzo, V.; De Petrocellis, L.; Appendino, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 467–471. (c) Allen, C. F.; Humphlett, W. J. *Can. J. Chem.* **1964**, *42*, 2616–2620. (d) Nair, D. P.; Podgórski, M.; Chatani, S.; Gong, T.; Xi, W.; Fenoli, C. R.; Bowman, C. N. *Chem. Mater.* **2014**, *26*, 724–744. (e) Krenske, E. H.; Petter, R. C.; Houk, K. N. *J. Org. Chem.* **2016**, *81*, 11726–11733.

(6) (a) Enders, D.; Saint-Dizier, A.; Lannou, M.-I.; Lenzen, A. *Eur. J. Org. Chem.* **2006**, 29–49. (b) Cristau, H.-J.; Vors, J.-P.; Christol, H. *Synthesis* **1979**, 538–541. (c) Tedeschi, L.; Enders, D. *Org. Lett.* **2001**,

DOI: 10.1021/acs.orglett.7b00720
Org. Lett. XXXX, XXX, XXX–XXX

3, 3515−3517. (d) Froestl, W.; Mickel, S. J.; Hall, R. G.; von Sprecher, G.; Strub, D.; Baumann, P. A.; Brugger, F.; Gentsch, C.; Jaekel, J. *J. Med. Chem.* **1995**, *38*, 3297−3312.
(7) (a) d'Angelo, J.; Revial, G.; Costa, P. R. R.; Castro, R. N.; Antunes, O. A. C. *Tetrahedron: Asymmetry* **1991**, *2*, 199−202. (b) Akinc, A.; Lynn, D. M.; Anderson, D. G.; Langer, R. *J. Am. Chem. Soc.* **2003**, *125*, 5316−5323. (c) Anderson, D. G.; Lynn, D. M.; Langer, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 3153−3158. (d) Lynn, D. M.; Amiji, M. M.; Langer, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1707−1710. (e) Vázquez, E.; Dewitt, D. M.; Hammond, P. T.; Lynn, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 13992−13993.
(8) Richardson, S. C. W.; Pattrick, N. G.; Stella Man, Y. K.; Ferruti, P.; Duncan, R. *Biomacromolecules* **2001**, *2*, 1023−1028.
(9) Ferruti, P.; Bianchi, S.; Ranucci, E.; Chiellini, F.; Caruso, V. *Macromol. Biosci.* **2005**, *5*, 613−622.
(10) Vernon, B.; Tirelli, N.; Bachi, T.; Haldimann, D.; Hubbell, J. A. *J. Biomed. Mater. Res., Part A* **2003**, *64A*, 447−456.
(11) (a) Lynn, D. M.; Langer, R. *J. Am. Chem. Soc.* **2000**, *122*, 10761−10768. (b) Lynn, D. M.; Anderson, D. G.; Putnam, D.; Langer, R. *J. Am. Chem. Soc.* **2001**, *123*, 8155−8156.
(12) The addition of HNu (such as R−OH, R_2NH, R−SH, etc.) to C═C bonds is one of the most desired transformations in organic synthesis due to the perfect atom economy. See: (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281. (b) Li, H.; Dong, K.; Jiao, H.; Neumann, H.; Jackstell, R.; Beller, M. *Nat. Chem.* **2016**, *8*, 1159−1166. For some other specific products, see: (c) Ramb, D. C.; Lerchen, A.; Kischkewitz, M.; Beutel, B.; Fustero, S.; Haufe, G. *Eur. J. Org. Chem.* **2016**, 1751−1759. (d) Liu, X.; Xu, C.; Wang, M.; Liu, Q. *Chem. Rev.* **2015**, *115*, 683−730.
(13) Some examples of Lewis acid catalyzed conjugate addition of indoles, thiols, and pyrroles with a,*β*-unsaturated ketone were reported. See: (a) Zhan, Z.-P.; Yang, R.-F.; Lang, K. *Tetrahedron Lett.* **2005**, *46*, 3859−3862. (b) Shi, M.; Cui, S.-C.; Li, Q.-J. *Tetrahedron* **2004**, *60*, 6679−6684. (c) Yadav, J. S.; Abraham, S.; Reddy, B. V. S.; Sabitha, G. *Synthesis* **2001**, 2165−2169. (d) Ji, S.-J.; Wang, S.-Y. *Synlett* **2003**, 2074−2076. (e) Bandini, M.; Cozzi, P. G.; Giacomini, M.; Melchiorre, P.; Selva, S.; Umani-Ronchi, A. *J. Org. Chem.* **2002**, *67*, 3700−3704.
(14) Bah, J.; Franzen, J. *Chem.−Eur. J.* **2014**, *20*, 1066−1072.
(15) Hu, X.; Martin, D.; Melaimi, M.; Bertrand, G. *J. Am. Chem. Soc.* **2014**, *136*, 13594−13597.
(16) (a) Feng, X.; Du, H. *Tetrahedron Lett.* **2014**, *55*, 6959−6964. (b) Mahdi, T.; Stephan, D. W. *J. Am. Chem. Soc.* **2014**, *136*, 15809−15812. (c) Scott, D. J.; Fuchter, M. J.; Ashley, A. E. *J. Am. Chem. Soc.* **2014**, *136*, 15813−15816. (d) Chatterjee, I.; Oestreich, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 1965−1968. (e) Mahdi, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2015**, *54*, 8511−8514. (f) Scott, D. J.; Simmons, T. R.; Lawrence, E. J.; Wildgoose, G. G.; Fuchter, M. J.; Ashley, A. E. *ACS Catal.* **2015**, *5*, 5540−5544. (g) Wang, W.; Meng, W.; Du, H. *Dalton Trans.* **2016**, *45*, 5945−5948.
(17) (a) Houghton, A. Y.; Hurmalainen, J.; Mansikkamaki, A.; Piers, W. E.; Tuononen, H. M. *Nat. Chem.* **2014**, *6*, 983−988. (b) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440−9441. (c) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090−3098.
(18) Simonneau, A.; Friebel, J.; Oestreich, M. *Eur. J. Org. Chem.* **2014**, 2077−2083.
(19) Harrison, D. J.; Edwards, D. R.; McDonald, R.; Rosenberg, L. *Dalton Trans.* **2008**, 3401−3411.
(20) Greb, L.; Tamke, S.; Paradies, J. *Chem. Commun.* **2014**, *50*, 2318−2320.
(21) (a) Maier, A. F.; Tussing, S.; Schneider, T.; Florke, U.; Qu, Z. W.; Grimme, S.; Paradies, J. *Angew. Chem., Int. Ed.* **2016**, *55*, 12219−12223. (b) Schulz, F.; Sumerin, V.; Leskela, M.; Repo, T.; Rieger, B. *Dalton Trans.* **2010**, *39*, 1920−1922.
(22) Kim, D. W.; Joung, S.; Kim, J. G.; Chang, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 14805−14809.
(23) (a) Ma, Y.; Wang, B.; Zhang, L.; Hou, Z. *J. Am. Chem. Soc.* **2016**, *138*, 3663−3666. (b) Oestreich, M.; Hermeke, J.; Mohr, J. *Chem. Soc. Rev.* **2015**, *44*, 2202−2220. (c) Simonneau, A.; Oestreich, M. *Nat. Chem.* **2015**, *7*, 816−822. (d) Gandhamsetty, N.; Park, S.; Chang, S. *J. Am. Chem. Soc.* **2015**, *137*, 15176−15184. (e) Chatterjee, I.; Qu, Z. W.; Grimme, S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 12158−12162.
(24) (a) Stephan, D. W. *Science* **2016**, *354*, 1248−1257. (b) Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 10018−10032. (c) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2015**, *54*, 6400−6441. (d) Piers, W. E.; Marwitz, A. J.; Mercier, L. G. *Inorg. Chem.* **2011**, *50*, 12252−12262. (e) Stephan, D. W. *Acc. Chem. Res.* **2015**, *48*, 306−316.
(25) (a) Tamke, S.; Qu, Z. W.; Sitte, N. A.; Florke, U.; Grimme, S.; Paradies, J. *Angew. Chem., Int. Ed.* **2016**, *55*, 4336−4339. (b) Ge, F.; Kehr, G.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2014**, *136*, 68−71. (c) Ge, F.; Kehr, G.; Daniliuc, C. G.; Mück-Lichtenfeld, C.; Erker, G. *Organometallics* **2015**, *34*, 4205−4208. (d) Hansmann, M. M.; Melen, R. L.; Rudolph, M.; Rominger, F.; Wadepohl, H.; Stephan, D. W.; Hashmi, A. S. *J. Am. Chem. Soc.* **2015**, *137*, 15469−15477. (e) Yu, Z.; Li, Y.; Shi, J.; Ma, B.; Liu, L.; Zhang, J. *Angew. Chem., Int. Ed.* **2016**, *55*, 14807−14811.

DOI: 10.1021/acs.orglett.7b00720
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