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Iridium- and Rhodium-Catalyzed C−H Activation and Formyl Alkynylation of Benzaldehydes under Chelation-Assistance

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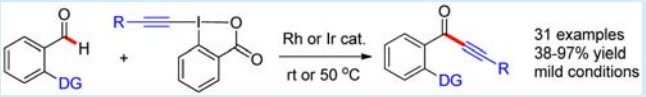
Supporting Information

ABSTRACT: Mild and efficient synthesis of ynones via Ir(III)- and Rh(III)-catalyzed, chelation-assisted formyl C−H alkynylation of benzaldehydes has been achieved using hypervalent iodine−alkyne reagents. Rhodium and iridium catalysis exhibited complementary substrate scope.



Ynones are important building blocks in synthetic chemistry owing to their high reactivity.[1] Typically, ynones were synthesized from the Sonogashira coupling of acid chlorides or from carbonylative Sonogashira coupling between aryl halides and terminal alkynes.[2,3] They are also accessible from the nucleophilic addition of metal alkynyl reagents to aldehyde followed by oxidation of the propargyl alcohols.[4] Alkynylation of the formyl group of aldehydes should be a more straightforward method since aldehydes are readily available.[5] This could be realized by metal-catalyzed C−H activation and functionalization of aldehyde.[6] However, aldehydes differ from arene substrates in C−H activation, and reports on direct functionalization of formyl groups are relatively limited.[7] This could be ascribable to the high reactivity of the carbonyl group but poor reactivity of the formyl C−H group. In addition, aldehydes are prone to side oxidation and decarbonylation, which may lower the efficiency of the reaction. Thus, metal-catalyzed C−H activation of formyl groups is mostly limited to insertion of formyl C−H bonds into unsaturated molecules such as alkenes and alkynes, among others, particularly under Rh(I) catalysis.[8]

Recently, it has been demonstrated that Rh(III) catalysts are highly efficient for the activation of sp^2 C−H bonds of arenes in the coupling with unsaturated molecules and with electrophilic reagents.[9] In the context of alkynylation, we[10] and others[11] have recently reported the Rh(III)- and Ir(III)-catalyzed C−H activation and alkynylation of a broad range of arenes using 1-(silylethynyl)-1,2-benziodoxol-3(1*H*)-ones (silyl-EBXs)[12] as an alkynylating reagent (Scheme 1).[13] Our mechanistic studies suggested that a Rh(III)−Rh(V)−Rh(III) mechanism might be operational in the alkynylation of 2-arylpyridines.[10a] To further extend the scope to other important C−H substrates, we reasoned that chelation-assisted C−H activation and alkynylation of benzaldehydes may lead to efficient synthesis of ynones. In this process, the conversion of an electrophilic formyl group into a nucleophilic metal−formyl bond represents metal-mediated umpolung of the carbonyl such that charge-matched coupling with electrophilic EBX reagents may proceed.

The use of OH and $NHSO_2R$ as directing group is practically useful.[14] We embarked on our studies with the screening of the reaction conditions for the coupling between salicylaldehyde and TIPS-EBX (Table 1). We initially applied $[RhCp^*Cl_2]_2$ as a catalyst in the presence of a base. However, no desired product was detected, and the salicylaldehyde was mostly recovered. Having noted that Rh(III) and Ir(III) catalysis can offer complementary substrate scope,[10a,15] we next resorted to the

Scheme 1. Metal-Catalyzed Alkynylation Reactions

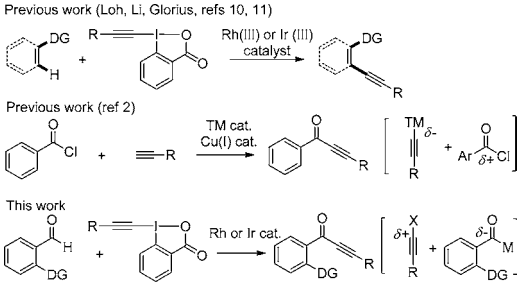
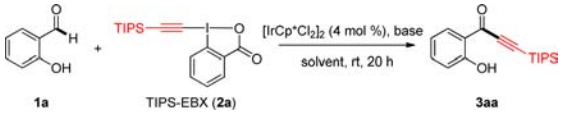


Table 1. Optimization Studies[a]



entry	base (equiv)	solvent	yield[b] (%)
1	CsOAc (2.0)	MeOH	52
2		MeOH	<5
3	CsOAc (0.5)	MeOH	62
4	CsOAc (1.2)	MeOH	77
5	CsOAc (1.2)	MeOH	43 (N_2)
6	NaOAc (1.2)	MeOH	58
7	CsOPiv (1.2)	MeOH	78
8	CsOAc (1.2)	DCE	42
9	CsOAc (1.2)	MeCN	13
10	CsOAc (1.2)	1,4-dioxane	75

[a]Reaction conditions: **1a** (0.2 mmol), TIPS-EBX (0.22 mol), $[Cp^*IrCl_2]_2$ (4 mol %), base, solvent (3 mL), under air at rt for 20 h. [b]Isolated yield after column chromatography.

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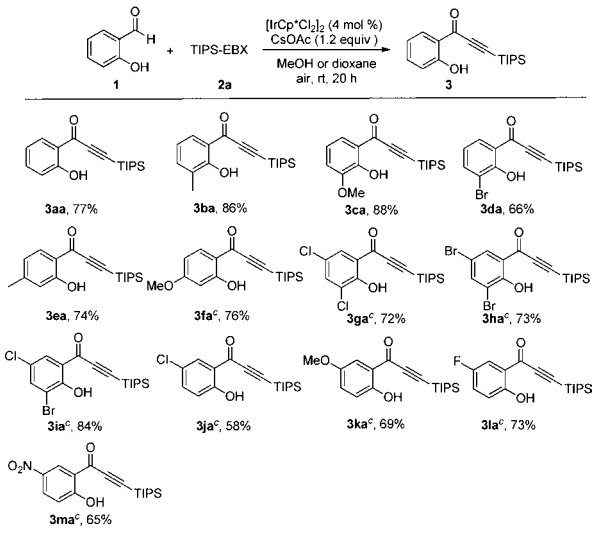
iridium congener $[IrCp^*Cl_2]_2$ as a catalyst. A desired coupling did occur without exclusion of air when CsOAc (2 equiv) was used as a base in MeOH, and product **3aa** was isolated in 52% yield (entry 1). Control experiments indicated that both a base additive and the catalyst are necessary. Variation of the amount of the CsOAc revealed that the yield reached optimum when CsOAc was used in a slightly superstoichiometric amount, under which conditions the product was isolated in 77% yield (entry 4). Screening of bases indicated that CsOPiv is equally optimal, but other bases such as NaOAc and Ag_2CO_3 led to poor conversions. Strong solvent effects have also been observed, and the reaction proceeded well in oxygenated solvents such as MeOH, ^{t}AmOH, or 1,4-dioxane, while MeCN and DCE are not suitable for this reaction (entries 8−10). Surprisingly, a sluggish reaction was observed (entry 5) when the reaction was performed under N_2, although no external oxidant seems necessary. This scenario has been observed in rhodium-catalyzed C−H activation of arenes bearing an oxidizing directing group.[16]

With the establishment of the optimal reaction conditions, we next investigated the scope and limitations of this reaction (Scheme 2). Under the optimal conditions, a broad scope of

Scheme 2. Ir(III)-Catalyzed C−H Alkynylation of Salicylaldehyde[a,b]



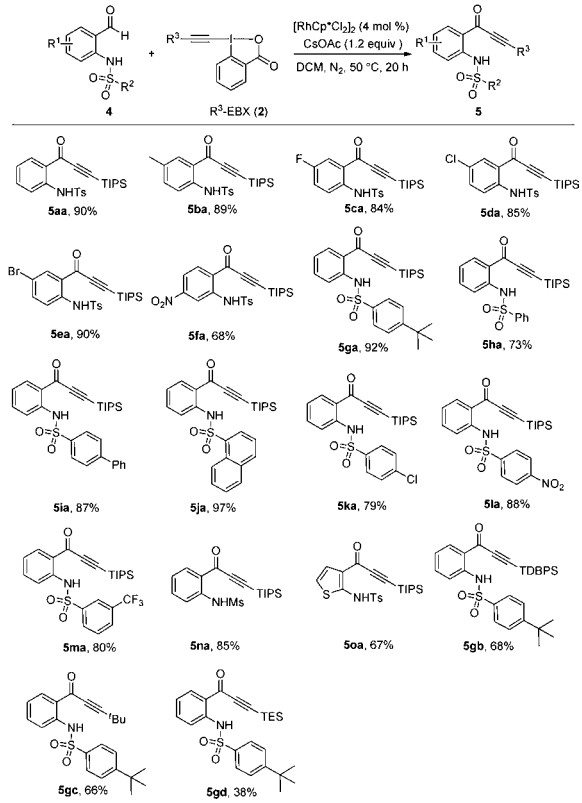
[a]Reaction conditions: aldehydes (0.20 mmol), TIPS-EBX (0.22 mmol), CsOAc (0.24 mmol), $[IrCp^*Cl_2]_2$ (0.008 mmol), MeOH (3.0 mL), rt, 20 h, sealed tube with air. [b]Isolated yield after column chromatography. [c]Reaction was performed in 1,4-dioxane.

salicylaldehydes is tolerated in the coupling with TIPS-EBX. When MeOH was used as the solvent, introduction of (weakly) electron-donating and halogen groups at the 3- and 4-positions of the benzene ring is tolerated. However, when substituents such as halogens, EDGs, and EWGs (halogen, NO_2) were introduced into the 3- and/or 5-position or when a 4-OMe was introduced, the reaction became sluggish, and only low yields were isolated. To our delight, switching the solvent to 1,4-dioxane regained the coupling efficiency. Thus, under these different conditions various substituents are compatible, and in all cases good to high isolated yields have been isolated by switching between these two solvents.

We next turned our attention to mild alkynylation of *N*-sulfonyl-2-aminobenzaldehydes. Although it is isostructural to salicylaldehyde, aldehyde **4g** failed to couple under the Ir-catalyzed conditions that are optimal for salicylaldehyde (see the Supporting Information). Importantly, switching the catalyst to $[RhCp^*Cl_2]_2$ gave rise to an efficient coupling (92% isolated yield) when the reaction was conducted in a halogenated solvent (DCM or DCE). In stark contrast to the reaction of salicylaldehydes, this reaction is much less efficient when air was not excluded.

By following the optimized conditions, a broad scope of *N*-sulfonyl-2-aminobenzaldehydes bearing different substituents (halogen, methyl, and nitro) all underwent smooth coupling with TIPS-EBX, and the product was isolated in 68−90% yield (Scheme 3). The sulfonyl group can be extended to

Scheme 3. Rh(III)-Catalyzed C−H Alkynylation of *N*-Sulfonyl-2-aminobenzaldehyde[a,b]



[a]Reaction conditions: *N*-sulfonyl 2-aminobenzaldehyde (0.20 mmol), R-EBX (0.22 mmol), CsOAc (0.24 mmol), $[RhCp^*Cl_2]_2$ (0.008 mmol), DCM (3.0 mL), 50 °C, 20 h, sealed tube under nitrogen. [b]Isolated yield after column chromatography.

methanesulfonyl and to benzenesulfonyls bearing different electron-donating and -withdrawing groups. Furthermore, the aldehyde backbone is not limited to benzaldehyde, and a 2-thenaldehyde also reacted to afford ynone **5oa** in 67% yield. The alkyne terminus in the EBX reagent can be expanded to other silyl groups (TES and TBDPS) and to a *tert*-Bu group albeit with relatively lower isolated yields. In contrast, poor or essentially no reaction occurred when TMS-EBX or Ph-EBX was employed, indicating that steric effect of the alkyne terminus is playing a significant role.[10,11,17]

To demonstrate the synthetic application of the alkynylation product, a simple derivatization reaction has been performed. K_2CO_3-promoted cyclization of ynone **3aa** in acetone led to the formation of chromone **6** in 84% yield (eq 1).[18] The substitution pattern of this product stays complementary to that obtained

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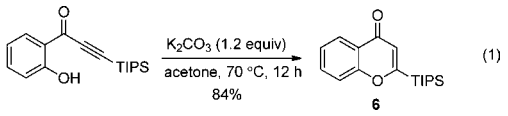
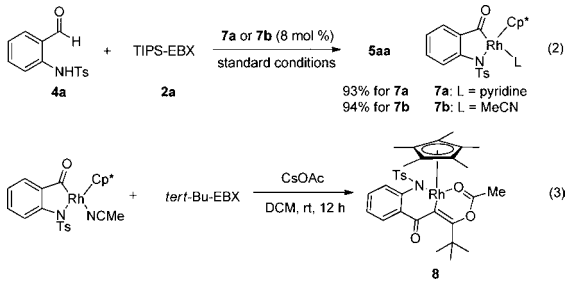
from rhodium-catalyzed oxidative coupling between salicylaldehyde and internal alkynes.[19]



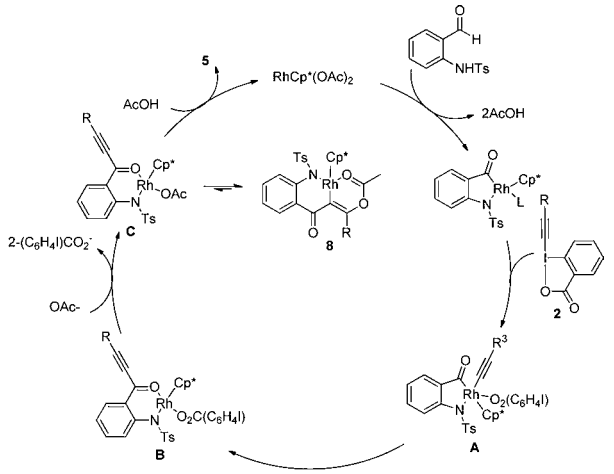
A series of experiments have been performed to probe the mechanism of alkynylation of *N*-Ts-2-aminobenzaldehyde. Intermolecular competition experiments revealed that a more electron-deficient *N*-sulfonyl-2-aminobenzaldehyde coupled at a higher rate (see the Supporting Information). To explore the relevancy of C−H activation, cyclometalated Rh(III) complexes **7a**,**b** stabilized by a nitrogen donor (pyridine and acetonitrile, respectively) have been prepared.[6h] Both complexes exhibited high catalytic activity, and the product **5aa** was isolated in excellent yield (eq 2), indicating that C−H activation is involved.



To further understand the interactions between the Rh−C bond and the alkynylating reagent, a stoichiometric reaction of **7b** and *t*-Bu-EBX has been performed in the presence of CsOAc, from which a Rh(III) tripodal complex **8** was isolated in 80% yield (eq 3). In fact, we have isolated an analogous tripodal complex in the stoichiometric reaction between a rhodacyclic complex and *t*-Bu-EBX.[10a] The structure of complex **8** was assigned on the basis of spectroscopic similarity with this analogous tripodal complex. Complex **8** proved to be an active catalyst (6 mol %) for the coupling of *N*-Ts-2-aminobenzaldehyde with TIPS-EBX, and the product **5aa** was isolated in 80% yield, a value comparable to that obtained by following the standard catalytic conditions. The fact that the tripodal complex is an active catalyst suggests that *β*-elimination of the acetate group should be reversible (vide infra).

On the basis of our preliminary results and our previous studies,[6h,10a] a catalytic cycle has been proposed starting from $RhCp^*(OAc)_2$ which proved to be an active catalyst (Scheme 4). Cyclometalation of *N*-Ts-2-aminobenzaldehyde affords a rhodacyclic intermediate **7**, to which the alkynylating reagent oxidatively adds to generate a Rh(V) intermediate **A**. We reasoned that this oxidative addition process could be more facile than that of the cationic rhodacycle $[RhCp^*(N\text{^}C)]^+$ derived from the cyclometalation of 2-arylpyridines because complexes **7a**,**b** are more electron-rich and is more prone to oxidation. Subsequent C(alkynyl)−C(acyl) reductive elimination affords a Rh(III) intermediate **B**, which undergoes substitution of the benzoate ligand by an acetate to give intermediate **C**. In the stoichiometric conditions without any substrate, reversible *β*-insertion of the acetate is followed to afford the stable tripodal intermediate **8** as an off-loop intermediate. In the real catalytic system, C(alkynyl)−C(acyl) reductive elimination is followed by subsequent protonolysis to furnish the coupled product together with regeneration of the active $RhCp^*(OAc)_2$ catalyst. The iridium-catalyzed alkynylation may follow a directly analogous mechanism.

Scheme 4. Proposed Catalytic Cycle



In summary, we have achieved rhodium- and iridium-catalyzed synthesis of ynones via C−H activation of benzaldehydes in the coupling with hypervalent iodine alkynylating reagents. An iridium(III) catalyst offered high activity for salicylaldehyde substrates, while a rhodium(III) catalyst is necessary when the substrate was switched to *N*-sulfonyl-2-aminobenzaldehydes. In these catalytic systems, the electrophilic aldehyde group is converted to a nucleophilic metal−formyl group, which matches the electrophilic EBX reagent. Preliminary mechanistic studies have been performed, and a plausible catalytic cycle has been proposed. Future work on the design and activation of other types of C−H bonds are underway in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, analytical data, and copies of NMR spectra of the products. This material is available free from charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews on ynones, see: (a) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874. (b) Arai, T.; Ikematsu, Y.; Suemitsu, Y. *Pure Appl. Chem.* **2010**, *82*, 1485. (c) Fraile, A.; Parra, A.; Tortosa, M.; Alemán, J. *Tetrahedron* **2014**, *70*, 9145. (d) Abbiati, G.; Arcadi, A.; Marinelli, F.; Rossi, E. *Synthesis* **2014**, *46*, 687.

(2) (a) Kakusawa, N.; Yamaguchi, K.; Kurita, J.; Tsuchiya, T. *Tetrahedron Lett.* **2000**, *41*, 4143. (b) Karpov, A. S.; Müller, T. J. J. *Org. Lett.* **2003**, *5*, 3451. (c) Chen, L.; Li, C.-J. *Org. Lett.* **2004**, *6*, 3151. (d) Alonso, D. A.; Nájera, C.; Pacheco, M. C. *J. Org. Chem.* **2004**, *69*, 1615. (e) Wang, B.; Bonin, M.; Micouin, L. *J. Org. Chem.* **2005**, *70*, 6126.

DOI: 10.1021/acs.orglett.5b00027
Org. Lett. 2015, 17, 920−923

(f) Willy, B.; Müller, T. J. J. *Arkivoc.* **2008**, *I*, 195. (g) D'Souza, D. M.; Müller, T. J. J. *Nat. Protoc.* **2008**, *3*, 1660.
(3) (a) Kobayashi, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1981**, 333. (b) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A* **1995**, *104*, 17. (c) Mohamed Ahmed, M. S.; Mori, A. *Org. Lett.* **2003**, *5*, 3057. (d) Karpov, A. S.; Merkul, E.; Rominger, F.; Müller, T. J. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6951. (e) Liang, B.; Huang, M.; You, Z.; Xiong, Z.; Lu, K.; Fathi, R.; Chen, J.; Yang, Z. *J. Org. Chem.* **2005**, *70*, 6097. (f) Liu, J.; Chen, J.; Xia, C. *J. Catal.* **2008**, *253*, 50. (g) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114. (h) Fusano, A.; Fukuyama, T.; Nishitani, S.; Inouye, T.; Ryu, I. *Org. Lett.* **2010**, *12*, 2410.
(4) (a) Jackson, M. M.; Leverett, C.; Toczko, J. F.; Roberts, J. C. *J. Org. Chem.* **2002**, *67*, 5032. (b) Annabelle, L. K.; Shi Shun, E. T.; Chernick, S. E.; Tykwinski, R. R. *J. Org. Chem.* **2003**, *68*, 1339. (c) Augé, J.; Lubin-Germain, N.; Seghrouchni, L. *Tetrahedron Lett.* **2003**, *41*, 819. (d) Praveen Rao, P. N.; Jashim Uddin, Md.; Knaus, E. E. *J. Med. Chem.* **2004**, *47*, 3972. (e) Ushijima, S.; Dohi, S.; Moriyama, K.; Togo, H. *Tetrahedron* **2012**, *68*, 1436. (f) Harigae, R.; Moriyama, K.; Togo, H. *J. Org. Chem.* **2014**, *79*, 2049.
(5) (a) Wang, Z.; Li, L.; Huang, Y. *J. Am. Chem. Soc.* **2014**, *136*, 12233. (b) Yuan, J.; Wang, J.; Zhang, G.; Liu, C.; Qi, X.; Lan, Y.; Miller, J. T.; Kropf, A. J.; Bunel, E. E.; Lei, A. *Chem. Commun.* **2015**, *51*, 576.
(6) (a) Willis, M. C. *Chem. Rev.* **2010**, *110*, 725. (b) Crépin, D.; Dawick, J.; Aïssa, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 620. (c) Chaplin, A. B.; Hooper, J. F.; Weller, A. S.; Willis, M. C. *J. Am. Chem. Soc.* **2012**, *134*, 4885. (d) Shi, Z.; Schröder, N.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 8092. (e) Wang, Z.; Li, X.; Huang, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 14219. (f) Zhou, B.; Yang, D.; Shi, J.; Feng, H.; Li, Y. *Chem.—Eur. J.* **2013**, *19*, 10511. (g) Jijy, E.; Prakash, P.; Shimi, M.; Pihko, P. M.; Joseph, N.; Radhakrishnan, K. V. *Chem.Commun.* **2013**, *49*, 7349. (h) Zhang, T.; Qi, Z.; Zhang, X.; Wu, L.; Li, X. *Chem.—Eur. J.* **2014**, *20*, 3283.
(7) For reviews, see: (a) Godula, K.; Sames, D. *Science* **2006**, *312*, 67. (b) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (c) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (d) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890. (e) Xu, L.-M.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712. (f) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (g) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780. (h) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (i) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (j) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879. (k) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788. (l) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (m) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (n) Yan, G.; Wu, X.; Yang, M. *Org. Biomol. Chem.* **2013**, *11*, 5558. (o) Ackermann, L. *Acc. Chem. Res.* **2014**, *47*, 281. (p) Zhang, F.; Spring, D. R. *Chem. Soc. Rev.* **2014**, *43*, 6906. (q) Huang, H.; Ji, X.; Wu, W.; Jiang, H. *Chem. Soc. Rev.* **2015**, DOI: 10.1039/C4CS00288A.
(8) For selected examples on Rh^{I}-catalyzed insertion of formyl C-H bonds into unsaturated molecules, see: (a) Tanaka, M.; Imai, M.; Yamamoto, Y.; Tanaka, K.; Shimowatari, M.; Nagumo, S.; Kawahara, N.; Suemune, H. *Org. Lett.* **2003**, *5*, 1365. (b) Osborne, J. D.; Randell-Sly, H. E.; Currie, G. S.; Cowley, A. R.; Willis, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 17232. (c) Shen, Z.; Dornan, P. K.; Khan, H. A.; Woo, T. K.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 1077. (d) Coulter, M. M.; Dornan, P. K.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 6932. (e) Phan, D. H. T.; Kim, B.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 15608. (f) Phan, D. H. T.; Kou, K. G. M.; Dong, V. M. *J. Am. Chem. Soc.* **2010**, *132*, 16354. (g) Parsons, S. R.; Hooper, J. F.; Willis, M. C. *Org. Lett.* **2011**, *13*, 998. (h) Murphy, S. K.; Bruch, A.; Dong, V. M. *Angew. Chem., Int. Ed.* **2014**, *53*, 2455.
(9) For recent reviews on Rh(III)-catalyzed C−H activation, see: (a) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimica Acta* **2012**, *45*, 31. (b) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814. (c) Satoh, T.; Miura, M. *Chem.—Eur. J.* **2010**, *16*, 11212. (d) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (e) Kuhl, N.; Schröder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443.
(10) (a) Xie, F.; Qi, Z.; Yu, S.; Li, X. *J. Am. Chem. Soc.* **2014**, *136*, 4780. (b) Zhang, X.; Qi, Z.; Gao, J.; Li, X. *Org. Biomol. Chem.* **2014**, *12*, 9329.
(11) (a) Feng, C.; Loh, T.-P. *Angew. Chem., Int. Ed.* **2014**, *53*, 2722. (b) Collins, K. D.; Lied, F.; Glorius, F. *Chem. Commun.* **2014**, *50*, 4459. (c) Feng, C.; Feng, D.; Loh, T.-P. *Chem. Commun.* **2014**, *50*, 9865. (d) Feng, C.; Feng, D.; Luo, Y.; Loh, T.-P. *Org. Lett.* **2014**, *16*, 5956.
(12) For the original synthesis of TIPS-EBX, see: Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Simonsen, A. J. *J. Org. Chem.* **1996**, *61*, 6547 The synthesis of EBX was improved by Waser and co-workers (ref 17b).
(13) For a review, see: Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299.
(14) (a) Li, J.-J.; Mei, T.-S.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 6452. (b) Lu, Y.; Wang, D.-H.; Engle, K. M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 5916. (c) Dai, H.-X.; Stepan, A. F.; Plummer, M. S.; Zhang, Y.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 7222.
(15) For iridium(III)-catalyzed C−H activation that is complementary to rhodium(III) catalysis, see: (a) Ueura, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2007**, *72*, 5362. (b) Itoh, M.; Hirano, K.; Satoh, T.; Shibata, Y.; Tanaka, K.; Miura, M. *J. Org. Chem.* **2013**, *78*, 1365. (c) Ryu, J.; Kwak, J.; Shin, K.; Lee, D.; Chang, S. *J. Am. Chem. Soc.* **2013**, *135*, 12861.
(16) (a) Zhang, X.; Chen, D.; Zhao, M.; Zhao, J.; Jia, A.; Li, X. *Adv. Synth. Catal.* **2011**, *353*, 719. (b) Too, P. C.; Noji, T.; Lim, Y. J.; Li, X.; Chiba, S. *Synlett* **2011**, 2789.
(17) (a) Brand, J. P.; Charpentier, J.; Waser, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 9346. (b) Brand, J. P.; Chevalley, C.; Scopelliti, R.; Waser, J. *Chem.—Eur. J.* **2012**, *18*, 5655. (c) Tolnai, G. L.; Ganss, S.; Brand, J. P.; Waser, J. *Org. Lett.* **2013**, *15*, 112. (d) Li, Y.; Brand, J. P.; Waser, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 6743.
(18) Harkat, H.; Blanc, A.; Weibel, J.-M.; Pale, P. *J. Org. Chem.* **2008**, *73*, 1620.
(19) Shimizu, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Chem.—Asian J.* **2008**, *3*, 881.

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