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ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · NOVEMBER 2013

Impact Factor: 12.11 · DOI: 10.1021/ja410195j · Source: PubMed

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Alkene Oxyalkylation Enabled by Merging Rhenium Catalysis with Hypervalent Iodine(III) Reagents via Decarboxylation

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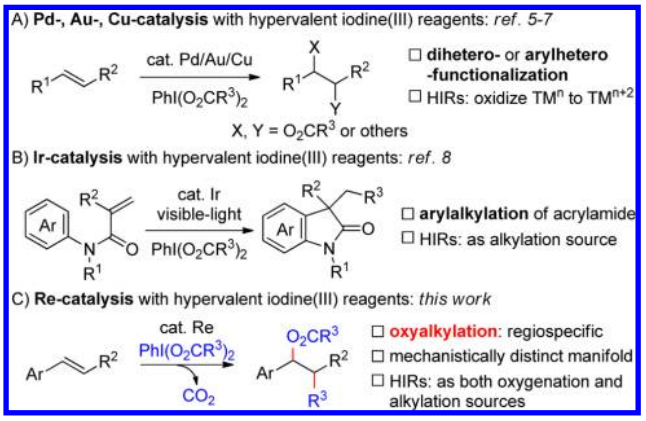
Supporting Information

ABSTRACT: Rhenium-catalyzed oxyalkylation of alkenes is described, where hypervalent iodine(III) reagents derived from widely occurring aliphatic carboxylic acids were used as, for the first time, not only an oxygenation source but also an alkylation source via decarboxylation. The reaction also features a wide substrate scope, totally regiospecific difunctionalization, mild reaction conditions, and ready availability of both substrates. Mechanistic studies revealed a decarboxylation/radical-addition/cation-trapping cascade operating in the reaction.

Alkene difunctionalizations are, among organic transformations, of the most prominent importance for efficient buildup of molecular complexity. They are highlighted by the Sharpless osmium-catalyzed dihydroxylations[1a] and aminohydroxylations.[1b] However, because the Os catalysts are expensive and highly toxic, alternative methods are needed to complement the Sharpless protocols and, more importantly, achieve greater reaction diversity.[2] Along this line, the use of hypervalent iodine(III) reagents (HIRs) in difunctionalization of alkenes has recently garnered significant attention owing to their ready accessibility, ease of handling, low cost, and environmentally benign character.[3,4] In these events, HIRs react commonly as electrophiles with olefins, leading to three-membered iodonium ions, and further act as excellent leaving groups to be replaced by other nucleophiles. The resulting reaction categories rely heavily on the limited types of key intermediates such as iodiranium and aziridinium ions.[4] Clearly, there is still a high demand for achieving the sought-after reaction diversity as well as regio- and stereocontrol on alkene difunctionalization with HIRs.

To meet this demand, the merging of transition-metal catalysis and HIRs has evolved as a powerful strategy to develop varied alkene difunctionalization reactions in the past few years.[5−8] For instance, Sorensen, Muñiz, Stahl, Sanford, and others elegantly demonstrated that palladium catalysis coupled with HIRs enables a wide range of alkene difunctionalizations, including amino-oxygenation,[5a−e] diamination,[5f−h] dioxygenation,[5i−k] amino-fluorination,[5l] and aryloxygenation,[5m−p] among others[5q−s] (Scheme 1A). Meanwhile, Muñiz[6a] and Nevado[6b] et al. successfully combined gold catalysis with HIRs, allowing for efficient alkene diamination, aminooxygenation, and arylamination. The groups of Seeyad and Chai,[7a] Blakey,[7b] and Chiba[7c] described the diacetoxylation and aminooxygenation of olefins by employing the binary system of copper catalysts and HIRs. Mechanistically, these transformations rely on the oxidation of low oxidation state metal species to high oxidation states (Pd^{II}/Pd^{IV}, Au^{I}/Au^{III}, and Cu^{I}/Cu^{III}) by hypervalent iodines to facilitate the formation of C−X bonds. Most recently, Zhu et al. disclosed an intramolecular alkylarylation of olefins by visible-light-promoted Ir-catalyzed decarboxylation of HIRs, though the reaction substrates were limited to 1,1-disubstituted *N*-arylacrylamides (Scheme 1B).[8] As part of our ongoing interest in rhenium catalysis and decarboxylation reactions,[9,10] here we report an unprecedented intermolecular decarboxylative oxyalkylation of alkenes enabled by the combination of Re catalysis with HIRs (Scheme 1C).[11] Remarkably, this reaction displays a mechanistically distinct manifold between HIRs and Re catalysts which is in contrast to those of other transition metals (e.g., Pd, Au, Cu, and Ir). It also represents the first example wherein HIRs act as both oxygenation and alkylation sources in the difunctionalizations of alkenes.

Scheme 1. Transition-Metal-Catalyzed Alkene Difunctionalizations with HIRs



At the outset, we selected 4-*tert*-butylstyrene **1c** and iodosobenzene diacetate **2a** as model substrates (Table 1). After an extensive survey of reaction parameters,[12] to our delight, the decarboxylative oxyalkylation product **3ca** was detected in 85% NMR yield after reaction with $Re_2(CO)_{10}$ as catalyst and

Received: October 4, 2013
Published: November 17, 2013

dx.doi.org/10.1021/ja410195j | J. Am. Chem. Soc. 2013, 135, 18048−18051

Table 1. Screening of Reaction Parameters[a]

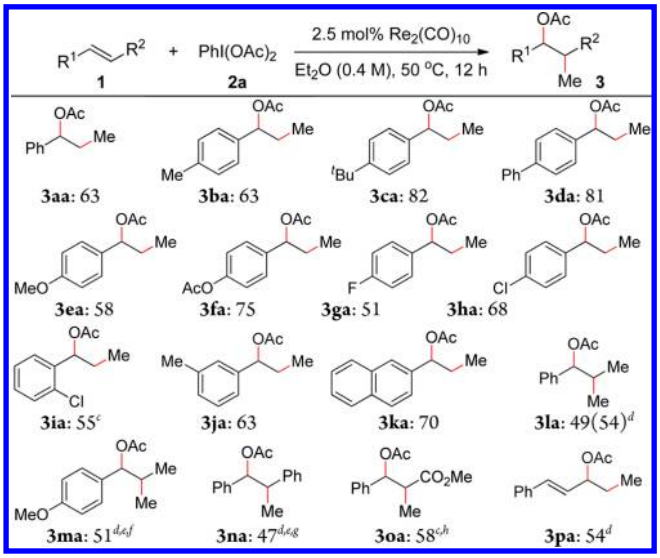
entry	cat. (5 mol%)	solvent	temp (°C)	yields (%)[b] 3ca	4ca	5ca
1	$Re_2(CO)_{10}$	Et_2O	80	85	6	4
2	–[c]	Et_2O	80	0	0	0
3	$ReCl(CO)_5$	Et_2O	80	72	13	3
4	$ReBr(CO)_5$	Et_2O	80	60	13	3
5	$[Re(CO)_3Br(thf)]_2$	Et_2O	80	77	7	3
6	$MnBr(CO)_5$	Et_2O	80	0	0	0
7	$Mn_2(CO)_{10}$	Et_2O	80	0	0	0
8[d]	$Sc(OTf)_3$	Et_2O	80	0	0	0
9[d]	$In(OTf)_3$	Et_2O	80	0	0	0
10[e]	$Re_2(CO)_{10}$	Et_2O	80	83	8	2
11[f]	**$Re_2(CO)_{10}$**	**Et_2O**	**50**	**83 (82)**[g]	**2**	**5**

[a]Reaction conditions unless otherwise noted: **1c** (0.2 mmol), **2a** (0.4 mmol), catalyst (0.01 mmol), solvent (1.0 mL), 12 h. [b]Determined by ^1H NMR analysis with an internal standard. [c]No catalyst. [d]Diacetoxylation product **6ca** was formed. [e]In dark. [f]2.5 mol% $Re_2(CO)_{10}$, 0.5 mL Et_2O. [g]Isolated yield on 0.5 mmol scale.

diethyl ether as solvent at 80 °C (entry 1). The concomitant formation of small amounts of oxidative Heck product **4ca** and alkene oxydimethylation product **5ca** was also observed in the reaction. Importantly, no products were formed in the absence of $Re_2(CO)_{10}$ (entry 2). Other Re catalysts gave inferior results, while manganese congeners showed no effectiveness at all (entries 3–7). Interestingly, traditional Lewis acids such as $Sc(OTf)_3$ and $In(OTf)_3$ merely formed the vicinal diacetoxylation product **6ca** (entries 8 and 9). Varying the solvents proved Et_2O to be optimal.[12] Notably, the reaction proceeded equally well when conducted in the dark, in contrast to the previous Ir system (entry 10).[8] Further optimizations demonstrated that the catalyst loading can be lowered to 2.5 mol% and the reaction temperature can be decreased to 50 °C at a higher concentration with no influence on the reaction outcome (entry 11).[12] Hence, **3ca** was obtained in 82% isolated yield with excellent chemo- and regioselectivity. Control experiments showed that byproducts **4ca** and **5ca** could not be generated from **3ca** nor **6ca** under the reaction conditions, which gave a hint on the possible reaction mechanism.[12]

With the optimized conditions in hand, we then examined the reactivity of various alkenes with $PhI(OAc)_2$ **2a** as the reaction partner (Scheme 2). It was shown that neither electron-donating nor -withdrawing groups on the benzene moieties had an obvious effect on the reaction outcome (**3aa**–**ha**). Among them, a range of functionalities including benzylic C–H bonds, ether, ester, and halogens were well tolerated in the reaction. *Ortho*- and *meta*-substituted aromatic alkenes also reacted smoothly with **2a**, leading to the expected products **3ia** and **ja**. Similarly, 2-vinylnaphthalene delivered the corresponding product **3ka** in good yield. Of note, no noticeable products were detected when aliphatic alkenes were used. Internal alkenes demonstrated a relatively sluggish reactivity; however, the expected products **3la**–**oa** could be obtained in synthetically valuable yields with slight modifications of reaction conditions. Remarkably, 1-phenyl-1,3-butadiene underwent a vicinal oxyalkylation on the terminal double bond, affording solely product **3pa** in a completely regioselective manner.

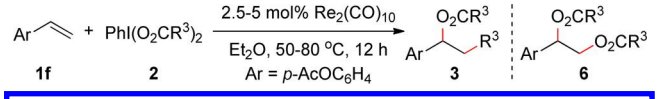
Scheme 2. Scope of Alkenes[a,b]

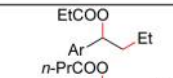
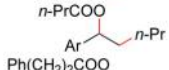
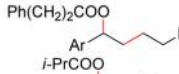
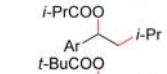
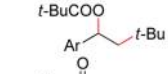
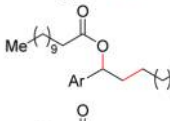
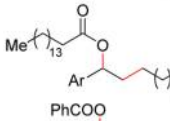
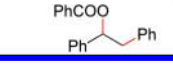


[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), $Re_2(CO)_{10}$ (0.0125 mmol), Et_2O (1.25 mL), 50 °C, 12 h. [b]Isolated yields of product **3** are shown. [c]2.5 mol% $ReCl(CO)_5$. [d]Visible light (15-W household bulb). [e]5.0 mol% $Re_2(CO)_{10}$, 80 °C. [f]Dioxygenation byproduct **6ma** was detected in 25% NMR yield (d.r. = 2:1). [g]Two diastereoisomers (*threo*:*erythro* = 3.4:1). [h]d.r. = 1.7:1.

Next, a range of HIRs were tested as shown in Table 2. Specifically, HIRs derived from primary, secondary, and tertiary aliphatic carboxylic acids were all well compatible with the alkene oxyalkylation protocol, affording the corresponding products **3fb**–**ff** smoothly. Note that visible light illumination by a

Table 2. Scope of HIRs[a]



entry	$PhI(O_2CR^3)_2$	product	yield (%)[b]
1	$PhI(O_2CEt)_2$ **2b**		**3fb**: 70[c]
2	$PhI(O_2C^nPr)_2$ **2c**		**3fc**: 71[d]
3	$PhI[O_2C(CH_2)_2Ph]_2$ **2d**		**3fd**: 55[d]
4	$PhI(O_2C^iPr)_2$ **2e**		**3fe**: 52[d]
5	$PhI(O_2C^tBu)_2$ **2f**		**3ff**: 65[d]
6	$PhI(O_2CC_{11}H_{23})_2$ **2g**		**3fg**: 45[d,e]
7	$PhI(O_2CC_{15}H_{31})_2$ **2h**		**3fh**: 43[f]
8	$PhI(O_2CPh)_2$ **2i**		**3ai**: 28[d,g]

[a]Reaction conditions: **1f** (0.5 mmol), **2** (1.0 mmol), $Re_2(CO)_{10}$ (0.025 mmol), Et_2O (1.0 mL), 80 °C, 12 h. [b]Isolated yields of product **3**. [c]2.5 mol% $Re_2(CO)_{10}$, Et_2O (1.25 mL), 50 °C. [d]Visible light (15-W household bulb). [e]**6fg**: 9% NMR yield. [f]**6fh**: 11% NMR yield. [g]**6ai**: 42% NMR yield.

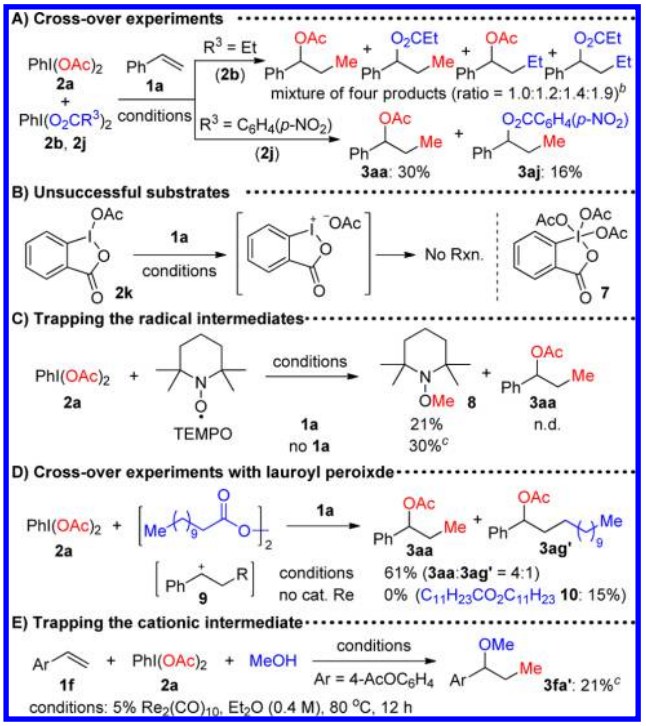
dx.doi.org/10.1021/ja410195j | J. Am. Chem. Soc. 2013, 135, 18048–18051

common household bulb was needed to enhance the reaction efficiency in some cases, which provides an additional handle to tune the reaction outcome. It should be pointed out that fatty acids are the key components in natural oils and fats, which represent the most important renewable raw materials for the chemical industry.[13] Hence, we subjected the HIRs **2g** and **2h**, derived from lauric acid and palmitic acid, respectively, to our reaction conditions. Gratifyingly, the long-chain oxyalkylation products **3fg** and **3fh** were successfully obtained in synthetically useful yields. In addition, when HIR resulting from benzoic acid was employed, the oxyarylation product **3ai** was obtained in low yield, with concurrent formation of alkene dioxygenation byproduct **6ai**, suggesting a likely radical decarboxylation mechanism.

To delve into the possible reaction mechanism, a series of experiments were conducted. Initially, the crossover experiments between two different HIRs were examined to ascertain whether the alkylation and oxygenation moieties originate from the same HIR molecule (Scheme 3A). It turned out that four hybrid products were obtained when equimolar amounts of HIRs **2a** and **2b** were treated with olefin **1a**, which implied a separate intermolecular alkylation/oxygenation might occur in the reaction. Interestingly, when HIRs **2a** and **2j** were subjected to the reaction conditions, only two products, **3aa** and **3aj**, arising from the decarboxylation of **2a** were formed, which showed that **2j** could participate in the oxygenation step despite its ineffectiveness in the decarboxylation step.[12] To differentiate the roles of two carboxylate groups in symmetrical HIRs (such as **2a**), the reaction of unsymmetrical substrate **2k** was then explored and failed to yield any oxyalkylation products (Scheme 3B). We speculated that heterolytic rather than homolytic breaking of the I−O bond of **2k** might take place first, resulting in the formation of acetate anion and cyclic iodonium cation, which are unable to decarboxylate in the reaction. In addition, Dess−Martin periodinane **7** exhibited no expected reactivity at all, which underlines the essential role of iodine(III) cores in substrates **2**.

To probe the nature of the decarboxylation step, the radical-trapping reagent TEMPO was added into the reaction of **1a** and **2a** (Scheme 3C). It was shown that the formation of product **3aa** was completely prohibited, and product **8** was obtained in 21% NMR yield, suggesting again a radical decarboxylation mechanism. Furthermore, the methyl radical could also be trapped by TEMPO in the absence of alkene **1a**. Considering that lauroyl peroxide can easily generate acyloxy radical and subsequent alkyl radical via decarboxylation,[14] we examined the crossover reaction of **2a** and lauroyl peroxide with alkene **1a** to gain insight into the nature of the ensuing oxygenation step after the alkyl radical addition to the alkene (Scheme 3D). It turned out that only two acetated products, **3aa** and **3ag′**, originating from decarboxylation of **2a** and lauroyl peroxide, respectively, were detected. No acyloxy radical-trapped products were formed, suggesting that the oxygenation step might occur through attack of a cationic intermediate **9** by the nucleophilic acetate anion (AcO^-). Importantly, formation of ester **10** instead of **3aa** and **3ag′** was detected in the absence of Re catalyst, indicating that Re is indispensable in generating cationic species **9**.[12,14] To further confirm the ionic character of the oxygenation step, an equimolar amount of methanol was added to the reaction of **1f** and **2a** (Scheme 3E). To our delight, product **3fa′**, arising from nucleophilic trapping of intermediate **9** by methanol, was obtained in 21% isolated yield, supporting our hypothesis.[12]

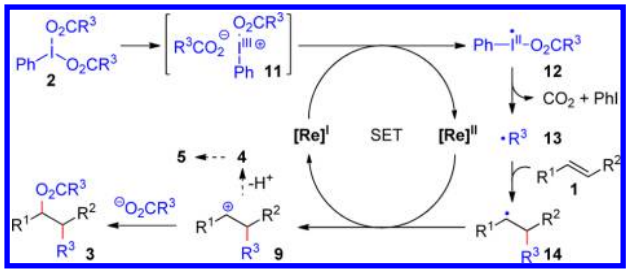
Scheme 3. Mechanistic Experiments[a]



[a]Yields determined by ^{1}H NMR analysis unless otherwise noted. [b]Determined by GC-MS. [c]Isolated yields.

Based on the above mechanistic studies, a possible reaction mechanism is depicted in Scheme 4. HIR **2** first undergoes a heterolytic cleavage of one I−O bond, giving cationic species **11**, which is reduced by Re^I catalyst, affording radical iodine intermediate **12**. Homolytic breaking of the remaining I−O bond in **12** could form PhI and an acyloxy radical, which suffers a decarboxylation process to generate alkyl radical **13** and release CO_2 simultaneously.[15] It is proposed that visible light might accelerate this decarboxylation step. Addition of alkyl radical **13** to alkene **1** would lead to radical intermediate **14**, which is oxidized by Re^{II} species to give cation **9** and regenerate Re^I species. Nucleophilic attack of **9** by a carboxylic anion would eventually result in the formation of product **3**, while elimination of a proton from **9** would afford the oxidative Heck byproduct **4** and the ensuing oxydialkylation byproduct **5**.

Scheme 4. Tentative Reaction Mechanism



In summary, we have developed an efficient process for oxyalkylation of simple alkenes by merging rhenium catalysts with HIRs derived from aliphatic carboxylic acids. It is the first time that HIRs are adopted as both alkylation and oxygenation sources in alkene difunctionalizations.[16] The wide substrate scope, excellent regioselectivity, mild reaction conditions, ease of

dx.doi.org/10.1021/ja410195j | J. Am. Chem. Soc. 2013, 135, 18048−18051

operation, and ready availability of simple olefins and aliphatic carboxylic acids add further benefits to this protocol. Mechanistic studies revealed a distinct manifold of Re catalysts with HIRs in this alkene oxyalkylation reaction, namely a decarboxylation/radical-addition/cation-trapping cascade. In light of the importance of fatty acids in sustainable chemistry,[13] implementation of this strategy of merging Re catalysts with HIRs for functionalization of unsaturated hydrocarbons holds promise in organic synthesis and is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Generous financial support from the National Natural Science Foundation of China (21002103, 21272238) and the National Basic Research Program of China (973 Program) (No. 2011CB808600) is gratefully acknowledged.

■ REFERENCES

(1) (a) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (b) Muñiz, K. *Chem. Soc. Rev.* **2004**, *33*, 166.

(2) For leading reviews on alkene difunctionalizations: (a) Kotov, V.; Scarborough, C. C.; Stahl, S. S. *Inorg. Chem.* **2007**, *46*, 1910. (b) Minatti, A.; Muñiz, K. *Chem. Soc. Rev.* **2007**, *36*, 1142. (c) Chemler, S. R.; Fuller, P. H. *Chem. Soc. Rev.* **2007**, *36*, 1153. (d) Jensen, K. H.; Sigman, M. S. *Org. Biomol. Chem.* **2008**, *6*, 4083. (e) Wolfe, J. P. *Synlett* **2008**, 2913. (f) McDonald, R. I.; Liu, G.; Stahl, S. S. *Chem. Rev.* **2011**, *111*, 2981. (g) Denmark, S. E.; Kuester, W. E.; Burk, M. T. *Angew. Chem., Int. Ed.* **2012**, *51*, 10938. (h) Wu, W.; Jiang, H. *Acc. Res. Chem* **2012**, *45*, 1736.

(3) For general reviews on HIRs: (a) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656. (b) Deprez, N. R.; Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924. (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299. (d) Ochiai, M.; Miyamoto, K. *Eur. J. Org. Chem.* **2008**, 4229. (e) Dohi, T.; Kita, Y. *Chem. Commun.* **2009**, 2073. (f) Uyanik, M.; Ishihara, K. *Chem. Commun.* **2009**, 2086. (g) Merritt, E. A.; Olofsson, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9052. (h) Liang, H.; Ciufolini, M. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 11849. (i) Ding, Q.; Ye, Y.; Fan, R. *Synthesis* **2013**, *45*, 1.

(4) For selected examples on metel-free alkene difunctionalizations with HIRs: (a) Boye, A. C.; Meyer, D.; Ingison, C. K.; French, A. N.; Wirth, T. *Org. Lett.* **2003**, *5*, 2157. (b) Correa, A.; Tellitu, I.; Domínguez, E.; SanMartin, R. *J. Org. Chem.* **2006**, *71*, 8316. (c) Wardrop, D. J.; Bowen, E. G.; Forslund, R. E.; Sussman, A. D.; Weerasekera, S. L. *J. Am. Chem. Soc.* **2009**, *132*, 1188. (d) Lovick, H. M.; Michael, F. E. *J. Am. Chem. Soc.* **2010**, *132*, 1249. (e) Fujita, M.; Yoshida, Y.; Miyata, K.; Wakisaka, A.; Sugimura, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 7068. (f) Röben, C.; Souto, J. A.; González, Y.; Lishchynskyi, A.; Muñiz, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 9478. (g) Kang, Y.-B.; Gade, L. H. *J. Am. Chem. Soc.* **2011**, *133*, 3658. (h) Zhong, W.; Yang, J.; Meng, X.; Li, Z. *J. Org. Chem.* **2011**, *76*, 9997. (i) Kim, H. J.; Cho, S. H.; Chang, S. *Org. Lett.* **2012**, *14*, 1424. (j) Farid, U.; Malmedy, F.; Claveau, R.; Albers, L.; Wirth, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 7018. (k) Liu, L.; Lu, H.; Wang, H.; Yang, C.; Zhang, X.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *Org. Lett.* **2013**, *15*, 2906. (l) Kong, W.; Feige, P.; de Haro, T.; Nevado, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 2469.

(5) For Pd catalysis with HIRs—Aminooxygenation: (a) Alexanian, E. J.; Lee, C.; Sorensen, E. J. *J. Am. Chem. Soc.* **2005**, *127*, 7690. (b) Liu, G.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 7179. (c) Desai, L. V.; Sanford, M. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5737. (d) Cui, S.; Wojtas, L.; Antilla, J. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 8927. (e) Chen, S.; Wu, T.; Liu, G.; Zhen, X. *Synlett* **2011**, *7*, 891. Diamination: (f) Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2005**, *127*, 14586. (g) Muñiz, K. *J. Am. Chem. Soc.* **2007**, *129*, 14542. (h) Martínez, C.; Muñiz, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 7031. Dioxygenation: (i) Li, Y.; Song, D.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 2962. (j) Wang, W.; Wang, F.; Shi, M. *Organometallics* **2010**, *29*, 928. (k) Neufeldt, S. R.; Sanford, M. S. *Org. Lett.* **2013**, *15*, 46. Aminofluorination: (l) Wu, T.; Yin, G.; Liu, G. *J. Am. Chem. Soc.* **2009**, *131*, 16354. Aryloxygenation: (m) Rodriguez, A.; Moran, W. *Eur. J. Org. Chem.* **2009**, 1313. (n) Jaegil, S.; Dufour, J.; Wei, H.; Piou, T.; Duan, X.; Vors, J.; Neuville, L.; Zhu, J. *Org. Lett.* **2010**, *12*, 4498. (o) Satterfield, A. D.; Kubota, A.; Sanford, M. S. *Org. Lett.* **2011**, *13*, 1076. (p) Matsura, B. S.; Condie, A. G.; Buff, R. C.; Karahalis, G. J.; Stephenson, C. R. J. *Org. Lett.* **2011**, *13*, 6320. Aryltrifluoromethylation: (q) Mu, X.; Wu, T.; Wang, H.-y.; Guo, Y.-l.; Liu, G. *J. Am. Chem. Soc.* **2012**, *134*, 878. Arylhalogenation: (r) Kalyani, D.; Sanford, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 2150. Bromooxygenation: (s) Yu, L.; Ren, L.; Yi, R.; Wu, Y.; Chen, T.; Guo, R. *Synlett* **2011**, *4*, 579.

(6) For Au catalysis with HIRs: (a) Iglesias, A.; Muñiz, K. *Chem.—Eur. J.* **2009**, *15*, 10563. (b) de Haro, T.; Nevado, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 906.

(7) For Cu catalysis with HIRs: (a) Seayad, J.; Seayad, A. M.; Chai, C. L. L. *Org. Lett.* **2010**, *12*, 1412. (b) Mancheno, D. E.; Thornton, A. R.; Stoll, A. H.; Kong, A.; Blakey, S. B. *Org. Lett.* **2010**, *12*, 4110. (c) Sanjaya, S.; Chiba, S. *Org. Lett.* **2012**, *14*, 5342.

(8) For Ir catalysis with HIRs: Xie, J.; Xu, P.; Li, H.; Xue, Q.; Jin, H.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2013**, *49*, 5672.

(9) For a leading review on Re catalysis: (a) Kuninobu, Y.; Takai, K. *Chem. Rev.* **2011**, *111*, 1938. For a leading review on decarboxylation: (b) Rodríguez, N.; Goossen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030.

(10) (a) Xia, D.; Wang, Y.; Du, Z.; Zheng, Q.-Y.; Wang, C. *Org. Lett.* **2012**, *14*, 588. (b) Tang, Q.; Xia, D.; Jin, X.; Zhang, Q.; Sun, X.-Q.; Wang, C. *J. Am. Chem. Soc.* **2013**, *135*, 4628. (c) Wang, C.; Piel, I.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 4194. (d) Wang, C.; Rakshit, S.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 14006.

(11) For selected carbooxygenation of alkenes without HIRs: (a) Kirchberg, S.; Fröhlich, R.; Studer, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 4235. (b) Kirchberg, S.; Fröhlich, R.; Studer, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 6877. (c) Ball, L. T.; Green, M.; Lloyd-Jones, G. C.; Russell, C. A. *Org. Lett.* **2010**, *12*, 4724. (d) Melhado, A. D.; Brenzovich, W. E.; Lackner, A. D.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 8885. (e) Brenzovich, W. E.; Brazeau, J. F.; Toste, F. D. *Org. Lett.* **2010**, *12*, 4728. (f) Tkatchouk, E.; Mankad, N. P.; Benitez, D.; Goddard, W. A., III; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 14293. (g) Liu, W.; Li, Y.; Liu, K.; Li, Z. *J. Am. Chem. Soc.* **2011**, *133*, 10756. (h) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Chem.—Eur. J.* **2012**, *18*, 2931. (i) Li, Y.; Studer, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 8221. (j) Hartmann, M.; Li, Y.; Studer, A. *J. Am. Chem. Soc.* **2012**, *134*, 16516.

(12) For more details, see Supporting Information.

(13) For a review: Biermann, U.; Friedt, W.; Lang, S.; Lühs, W.; Machmüller, G.; Metzger, J. O.; Rüsch gen. Klaas, M.; Schäfer, H. J.; Schneider, M. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2206.

(14) Ryzhkov, L. R. *J. Org. Chem.* **1996**, *61*, 2801.

(15) (a) Sandin, R. B.; McCormack, W. B. *J. Am. Chem. Soc.* **1945**, *67*, 2051. (b) Leffler, J.; Story, L. *J. Am. Chem. Soc.* **1967**, *89*, 2333. (c) Concepcion, J. I.; Francisco, C. G.; Freire, R.; Hernandez, R.; Salazar, J. A.; Suarez, E. *J. Org. Chem.* **1986**, *51*, 402. (d) Minisci, F.; Vismara, E.; Fontana, F.; Claudia Nogueira Barbosa, M. *Tetrahedron Lett.* **1989**, *30*, 4569. (e) Togo, H.; Katohgia, M. *Synlett* **2001**, 565. (f) Wu, T.; Zhang, H.; Liu, G. *Tetrahedron* **2012**, *68*, 5229.

(16) Of note, the alkylation of alkenes using alkyl halides or alkylmetal reagents is often nontrivial due to the β-H elimination issue. For selected examples, see: (a) de Armas, J.; Hoveyda, A. H. *Org. Lett.* **2001**, *3*, 2097. (b) Firmansjah, L.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 11340. (c) Urkalan, K. B.; Sigman, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 18042.