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Oxidation and Amination of Benzylic sp^3 C−H Bond Catalyzed by Rhenium(V) Complexes

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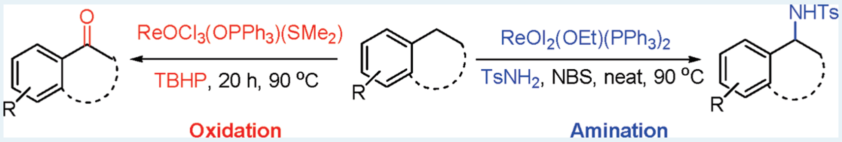
S *Supporting Information*



ABSTRACT: An efficient method for the oxidation of benzylic sp^3 C−H bond to produce ketones or esters using rhenium(V) complexes as catalysts has been developed. Moreover, the amination of benzylic sp^3 C−H bond with NH_2Ts in the presence of NBS has also been reported in moderate to good yields under the catalyst of rhenium(V)-based complexes.

KEYWORDS: *C−H activation, oxidation, amination, rhenium complexes, transition metal catalysis*

Direct C−H bond activation based on transition metal catalysis provides a straightforward method for the synthesis of valuable heteroatom-containing compounds and also represents one of the formidable challenges in organic chemistry.[1−6] Oxidation and amination of a saturated sp^3 C−H bond can quickly install an oxygen atom or an amino group on a carbon atom and have attracted considerable attention, since most of the known drugs and natural products are oxygen- and nitrogen-containing compounds.[7−9]

Initially, Cr(VI)-[10] or Mn(VII)-based[11] reagents were employed in the reactions of the oxidation of benzylic sp^3 C−H bond either in stoichiometric or excess quantities. Recently, several protocols for sp^3 C−H bond oxidation catalyzed by transition metal complexes, such as Ru, Rh, and Au etc.,[12−28] have been reported. In addition, amination of sp^3 C−H bond with simple amides via transition metal catalysts has been developed.[29−46]

Although methyltrioxorhenium is an efficient oxidation transformation catalyst,[47−51] the difficult availability and expensive nature limits its further applications in organic catalytic reactions. Therefore, it is of significance to develop more facile syntheses of different valence rhenium catalysts. Toste and Abu-Omar et al. reported a variety of high-valence rhenium oxo and imido complexes, which have shown efficient activities in catalytic reduction reaction.[52− 57] Moreover, Kuninobu and Takai have developed low-valence rhenium(I) complexes for the direct sp^2 C−H bond activation process.[58−67] To the best of our knowledge, there have been few reports on sp^3 C−H bond activation reaction under the catalysis of high-valence, low toxicity, and air-stable rhenium complexes.[68] Until now, only a few examples of C−H bond oxidation[69,70] and none of the amination reaction catalyzed by rhenium(V) complexes have been reported. In this paper, we report the oxidation and amination reactions of the benzylic sp^3 C−H bond based on high-valence rhenium(V) catalysts.

In the first series of experiments, diphenylmethane was chosen as the model substrate. We investigated the optimization reaction conditions, including the solvents, temperature, rhenium catalysts, and oxidants. The results are summarized in Table 1. When dichloromethane (DCM), 1,2-dichloroethane (DCE), and acetonitrile (MeCN) were used as the solvent in the presence of 5 mol % of $ReOCl_3(OPPh_3)(SMe_2)$ at 60 °C, no corresponding product was observed (entries 1−3). The product could be obtained in 21% and 35% yield when 10 and 20 mol % of pyridine was used in MeCN (entries 4−5). When the reaction was tested in pyridine, the yield was increased to 64% (entry 6). During this process, pyridine may play two roles: ligand and solvent. When the reaction temperature was increased to 90 °C, the yield increased to 97% (entry 7). After testing different rhenium catalysts, such as $[n\text{-}Bu_4N][ReO_4]$, $ReOCl_3(PPh_3)_2$, $ReO_2I(PPh_3)_2$, and $ReOI_2(OEt)(PPh_3)_2$, we found that $ReOCl_3(OPPh_3)(SMe_2)$ exhibits the most effective catalyst (entries 7−11). The result of screening of different oxidants indicated that TBHP could play a pivotal role for the high efficiency of the desired product (entries 12−13). The reaction was absent in the absence of the rhenium catalysts (entry 14).

Having established the optimal reaction conditions, a wide range of benzylic reagents were tested to explore the generality of this oxidation transformation. The reactions were conducted with 5 mol % of $ReOCl_3(OPPh_3)(SMe_2)$ and 2 equiv of TBHP

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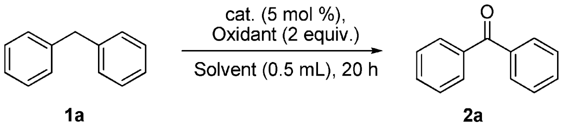
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	oxidant	temp (°C)	solvent	yield (%)[b]
1	$ReOCl_3(OPPh_3)(SMe_2)$	70% TBHP (aq.)	60	DCM	N. R.
2	$ReOCl_3(OPPh_3)(SMe_2)$	70% TBHP (aq.)	60	DCE	N. R.
3	$ReOCl_3(OPPh_3)(SMe_2)$	70% TBHP (aq.)	60	CH_3CN	N. R.
4[c]	$ReOCl_3(OPPh_3)(SMe_2)$	70% TBHP (aq.)	60	CH_3CN	21
5[d]	$ReOCl_3(OPPh_3)(SMe_2)$	70% TBHP (aq.)	60	CH_3CN	35
6	$ReOCl_3(OPPh_3)(SMe_2)$	70% TBHP (aq.)	60	pyridine	63
7	$ReOCl_3(OPPh_3)(SMe_2)$	70% TBHP (aq.)	90	pyridine	97
8	$ReO_2I(PPh_3)_2$	70% TBHP (aq.)	90	pyridine	52
9	$ReOCl_3(PPh_3)_2$	70% TBHP (aq.)	90	pyridine	24
10	$[n\text{-}Bu_4N][ReO_4]$	70% TBHP (aq.)	90	pyridine	43
11	$ReOI_2(OEt)(PPh_3)_2$	70% TBHP (aq.)	90	pyridine	59
12	$ReOCl_3(OPPh_3)(SMe_2)$	H_2O_2	90	pyridine	N. R.
13	$ReOCl_3(OPPh_3)(SMe_2)$	O_2	90	pyridine	N. R.
14	no catalysts	70% TBHP (aq.)	90	pyridine	<10%

[a] All reactions were performed on a 0.5 mmol scale of substrate with 2 equiv of oxidant in 0.5 mL of solvent. [b] Isolated yields. [c] 10 mol % of pyridine was used. [d] 20 mol % of pyridine was used.

in 0.5 mL of pyridine at 90 °C for 20 h. As shown in Table 2, all substrates accomplished the reaction smoothly, and the corresponding products were obtained in moderate to excellent yields. We found that diphenylmethane type substrates gave the corresponding products in excellent yields (entries 1−3). Less activated substrates with one annelated aryl group or one heteroaryl group in a cyclic structure led to benzylic oxidation products in moderate yields between 61% and 76% (entries 4−6). The ethylbenzene substituents could also be oxidized to form the corresponding acetophenones in moderate to good yields (entries 7−10). When phenyl propane and phenyl butane were tested, only moderated yields were obtained (entries 11, 12). The isobutylbenzene resulted in a lower yield in comparison with ethylbenzene (34% vs 88%), which may be due to the steric effect (entries 7, 13). Cyclohexane was also tested under the optimal reaction conditions; however, the result was not as positive as presented above (entry 14).

Inspired by the above good results of the benzylic sp^3 C−H bond oxidation, we further drew our attention to the amination of benzylic sp^3 C−H bond by using various rhenium(V) catalysts. Amination of the sp^3 C−H bond could be achieved by direct insertion of nitrene (TsN=IPh, etc.)[7,13,20] or in situ-generated nitrene arising from the oxidation of amide ($TsNH_2/PhI(OAc)_2$, NBS/$TsNH_2$, etc.).[71−74] In our reaction, diphenylmethane was chosen as the substrate for the optimization of the catalysis protocol using the aforementioned methods. As shown in Table 3, while using $ReOI_2(OEt)(PPh_3)_2$ as the catalyst, we found that the combination of $TsNH_2$ and NBS proved to be the most efficient amination reagent (entries 1−3). Then various rhenium-based catalysts were screened, and $ReOI_2(OEt)(PPh_3)_2$ was found to be the most efficient catalyst for this transformation (entries 4−8). Instead of amination product, bromodiphenylmethane was formed under the none-catalyzed conditions (entry 9). However, bromodiphenylmethane was subjected to the catalytic condition of the reaction, and no amination products were formed.

With the optimized reaction conditions in hand, we investigated the scope of this protocol using $TsNH_2$ as the N source and $ReOI_2(OEt)(PPh_3)_2$ as the catalyst (Table 4). It was found that diarylmethylene could afford the corresponding product in excellent yield up to 94% (entry 1). The aryl group in a cyclic system and the ethylbenzene derivatives gave the amination products in moderate yields (entries 3−6). When the unactivated cyclohexane was tested, no corresponding product was obtained (entry 7).

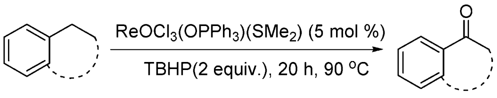
The plausible mechanism for the amination of sp^3 C−H bond catalyzed by $ReOI_2(OEt)(PPh_3)_2$ was shown in Scheme 1. The $TsNH_2$ presumably first reacts with NBS to afford the *N*-bromosulfonamide A, then A undertakes proton exchange with the catalyst to give the intermediate complex B, which then further produces a rhenium-nitrene intermediate C via bromine transfer. C combines with the sp^3 C−H bond of the benzylic substrate to form the transition state D. After the splitting of the N=Re bond of D, the corresponding amination product could be obtained, and the complex E would complete the catalytic cycle. Further investigation by introducing radical scavengers I_2 and BHT does not quench the reaction, ruling out the radical feature of the reaction.

In summary, we have developed a facile method for the oxidation of the benzylic sp^3 C−H bond with $ReOCl_3(OPPh_3)(SMe_2)$ as catalyst and TBHP as oxidant in a pyridine solution. Furthermore, we have also described a simple, convenient, and practical method for the amination of the benzylic sp^3 C−H bond with NH_2Ts in the presence of NBS under the catalysis of $ReOI_2(OEt)(PPh_3)_2$. These transformations proceed in moderate to good yields for a wide range of benzylic compounds. This novel reactivity of rhenium catalysts suggests that high-valence rhenium(V) complexes could catalyze sp^3 C−H bond activation reactions efficiently. Further studies on the C−H bond activation reaction mechanisms catalyzed by high-valence rhenium(V) complexes are under way in our laboratory.

■ EXPERIMENTAL SECTION

Representative Procedure for the Benzylic Oxidation: Conversion of Diphenylmethane. A Schlenk flask was charged with $ReOCl_3(OPPh_3)(SMe_2)$ (16 mg, 5 mol %), pyridine (0.5 mL), and diphenylmethane (84 mg, 0.5 mmol). After the

Table 2. $ReOCl_3(OPPh_3)(SMe_2)$-Catalyzed Benzylic Oxidation[a]



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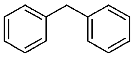
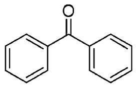
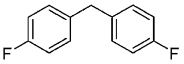
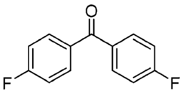
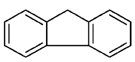
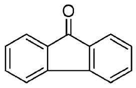
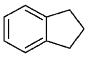
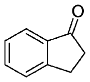
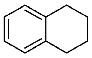
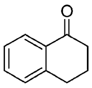
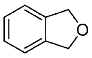
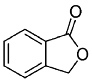
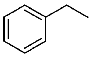
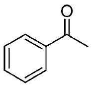
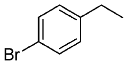
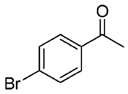
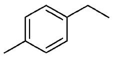
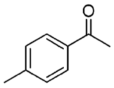
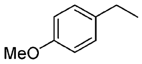
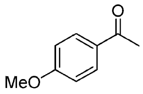
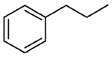
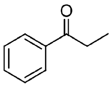
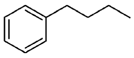
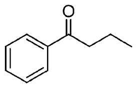
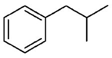
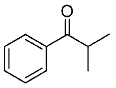
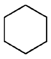
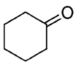
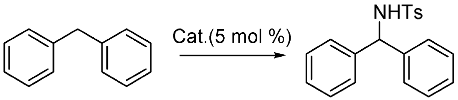
Entry	Substrate	Product		Yield(%)[b]
1			2a	97
2			2b	95
3			2c	96
4			2d	61
5			2e	69
6			2f	76
7			2g	88
8			2h	68
9			2i	60
10			2j	91
11			2k	52
12			2l	58
13			2m	34
14			2n	N.R.

[a] All reactions were performed on a 0.5 mmol scale of substrates with 5 mol % catalyst and 2 equiv of 70% TBHP in 0.5 mL of pyridine at 90 °C for 20 h. [b] Isolated yields.

Table 3. Rhenium Base-Catalyzed Diphenylmethane Amination[a]

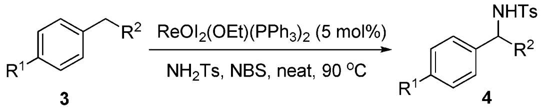


3a 4a

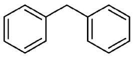
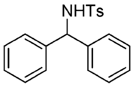
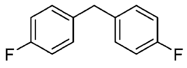
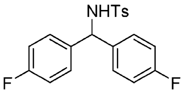
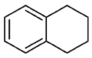
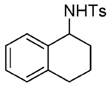
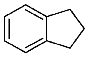
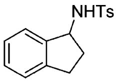
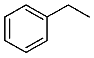
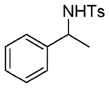
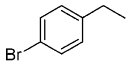
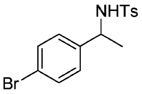
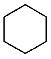
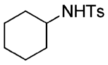
entry	catalyst	method[b]	yield (%)[c]
1	$ReOI_2(OEt)(PPh_3)_2$	A	58
2	$ReOI_2(OEt)(PPh_3)_2$	B	64
3	$ReOI_2(OEt)(PPh_3)_2$	C	94
4	$KReO_4$	C	65
5	NH_4ReO_4	C	78
6	$ReOCl_3(OPPh_3)(SMe_2)$	C	83
7	$[^nBu_4N][ReOCl_4]$	C	83
8	$ReO_2I(PPh_3)_2$	C	66
9[d]	no catalysts	C	

[a] All reactions were performed on a 0.25 mmol scale of amine with 0.05 mol % catalyst. [b] Method A: Reaction was performed at 50 °C for 1 day with a catalyst/amine/$PhI(OAc)_2$ molar ratio of 1:20:60. Method B: Reaction was performed at 90 °C for 20 h with a catalyst/N-source (PhI=NTs) molar ratio of 1:20. Method C: Reactions were performed at 90 °C for 1 day with a catalyst/amine/NBS molar ratio of 1:20:30. [c] Isolated yields, based on the amount of amine. [d] No amination product was detected, but bromodiphenylmethane was formed.

Table 4. $ReOI_2(OEt)(PPh_3)_2$ Catalyzed Amination of Benzylic sp^3 C−H Bonds[a]



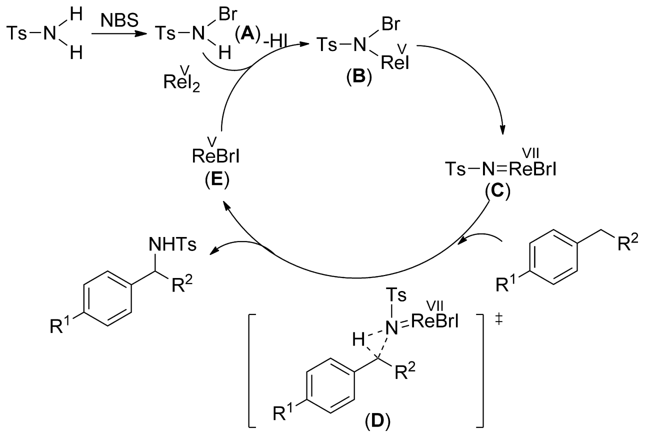
3 4

Entry	Substrate	Product		Yield(%)[b]
1			4a	94
2			4b	84
3			4c	69
4			4d	67
5			4e	60
6			4f	69
7			4g	N.R.

[a] Reaction was performed at 90 °C for 20 h with a catalyst/amine/NBS molar ratio of 1:20:30. [b] Isolated yields, based on the amount of amine.

addition of TBHP (70% in H_2O; 130 μL, 1 mmol), the reaction mixture was heated at 90 °C for 20 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aqueous HCl (10 mL) to remove the pyridine. The organic phase was extracted with Et_2O (3 × 10 mL), washed with brine, and dried by Na_2SO_4. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining

Scheme 1. Mechanism of Rhenium Catalyzed Amination of Benzyl sp^3 C−H Bond



mixture was separated by column chromatography (silica gel; ethyl acetate/petroleum ether = 1:20 as eluent), affording benzophenone; yield: 88 mg (97%).

Representative Procedure for the Benzylic Amination: Conversion of Diphenylmethane. A Schlenk flask was charged with $ReOI_2(OEt)(PPh_3)_2$ (13 mg, 5 mol %), NBS (54 mg, 0.3 mmol), and NH_2Ts (43 mg, 0.25 mmol). After the addition of diphenylmethane (1 mL), the reaction mixture was heated at 90 °C for 20 h. The mixture was then allowed to cool to room temperature and separated by column chromatography (silica gel; ethyl acetate/petroleum ether = 1: 5 as eluent), affording the desired product; yield: 79 mg (94%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General procedure for the preparation of ketones and amines, ^{1}H NMR spectroscopic data, and spectra for all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712.
(2) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147.
(3) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624.
(4) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094.
(5) Wang, D.-H.; Engle, K. M.; Shi, B.-F.; Yu, J.-Q. *Science* **2010**, *327*, 315.
(6) Li, Z.-P.; Li, C.-J. *J. Am. Chem. Soc.* **2005**, *127*, 3672.
(7) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242.
(8) Collet, F.; Dodd, R. H.; Dauban, P. *Chem. Commun.* **2009**, 5061.
(9) Li, Z.-P.; Yu, R.; Li, H.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 7497.
(10) Muzart, J. *Tetrahedron Lett.* **1987**, *28*, 3139.
(11) Zhao, D.; Lee, D.-G. *Synthesis* **1994**, 915.
(12) Retchera, B.; Costa, J.-S.; Tang, J.; Hage, R.; Gameza, P.; Reedijk, J. *J. Mol. Catal. A: Chem.* **2008**, *286*, 1.
(13) Nakanishi, M.; Bolm, C. *Adv. Synth. Catal.* **2007**, *349*, 861.
(14) Li, S.-J.; Wang, Y.-G. *Tetrahedron Lett.* **2005**, *46*, 8013.
(15) Rosenthal, J.; Luckett, T. D.; Hodgkiss, J. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 6546.
(16) Murahashi, S. I.; Komiya, N.; Oda, Y.; Kuwabara, T.; Naota, T. *J. Org. Chem.* **2000**, *65*, 9186.
(17) Burri, E.; Öhm, M.; Daguenet, C.; Severin, K. *Chem.—Eur. J.* **2005**, *11*, 5055.
(18) Kamata, K.; Kasai, J.; Yamaguchi, K.; Mizuno, N. *Org. Lett.* **2004**, *6*, 3577.
(19) Catino, A. J.; Forslund, R. E.; Doyle, M. P. *J. Am. Chem. Soc.* **2004**, *126*, 13622.
(20) Catino, A. J.; Nichols, J. M.; Choi, H.; Gottipamula, S.; Doyle, M. P. *Org. Lett.* **2005**, *7*, 5167.
(21) Gorden, A. E. V.; Wu, X.-H. *Eur. J. Org. Chem.* **2009**, 503.
(22) Valusamy, S.; Punniyamurthy, T. *Tetrahedron Lett.* **2003**, *44*, 8955.
(23) Nechab, M.; Einhorn, C.; Einhorn, J. *Chem. Commun.* **2004**, 1500.
(24) Bonvin, Y.; Callens, E.; Larrosa, I.; Henderson, D. A.; Oldham, J.; Burton, A. J.; Barrett, A. G. M. *Org. Lett.* **2005**, *7*, 4549.
(25) Modica, E.; Bombieri, G.; Colombo, D.; Marchini, N.; Ronchetti, F.; Scala, A.; Toma, L. *Eur. J. Org. Chem.* **2003**, 2964.
(26) Jurado-Gonzalez, M.; Sullvian, A. C.; Wilson, J. R. H. *Tetrahedron Lett.* **2003**, *44*, 4283.
(27) Minisci, F.; Punta, C.; Recupero, F.; Fontana, F.; Pedulli, G. F. *J. Org. Chem.* **2002**, *67*, 2671.
(28) Li, H.-R.; Li, Z.-P.; Shi, Z. J. *Tetrahedron* **2009**, *65*, 1856.
(29) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293.
(30) Wang, Z.; Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Org. Lett.* **2008**, *10*, 1863.
(31) Prokopcová, H.; Bergman, S. D.; Aelvoet, K.; Smout, V.; Herrebout, W.; Veken, B. V.; Meerpoel, L.; Maes, B. U. W. *Chem.—Eur. J.* **2010**, *16*, 13063.
(32) Au, S.-M.; Huang, J.-S.; Che, Z.-M.; Yu, W.-Y. *J. Org. Chem.* **2000**, *65*, 7858.
(33) Huard, K.; Lebel, H. *Chem.—Eur. J.* **2008**, *14*, 6222.
(34) Guo, C.; Song, J.; Luo, S.-W.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2010**, *49*, 5558.
(35) Fructos, M. R.; Trofimenko, S.; Díaz-Requejo, M. M.; Pérez, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 11784.
(36) Jazzar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem.—Eur. J.* **2010**, *16*, 2654.
(37) Thu, H.-Y.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9048.
(38) Cui, Y.; He, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 4210.
(39) Li, Z.-G.; Capretto, D. A.; Rahaman, R.; He, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 5184.
(40) Li, Z.-G.; Capretto, D. A.; Rahaman, R. O.; He, C. *J. Am. Chem. Soc.* **2007**, *129*, 12058.
(41) Liu, Y.-G.; Wei, J. H.; Che, C. M. *Chem. Commun.* **2010**, *46*, 6926.
(42) Liu, Y.-G.; Che, C. M. *Chem.—Eur. J.* **2010**, *16*, 10494.
(43) King, E. R.; Hennessy, E. T.; Betley, T. A. *J. Am. Chem. Soc.* **2011**, *133*, 4917.
(44) King, E. R.; Betley, T. A. *Inorg. Chem.* **2009**, *48*, 2361.
(45) Lyaskovskyy, V.; Suarez, A. I. O.; Lu, H.-J.; Zhang, X. P.; de Bruin, B. *J. Am. Chem. Soc.* **2011**, *133*, 12264.
(46) Lu, H.-J.; Jiang, H.-L.; Wojtas, L.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2010**, *49*, 10192.
(47) Kühn, F. E.; Santos, A. M.; Gonçalves, I. S.; Romão, C. C.; Lopes, A. D. *Appl. Organomet. Chem.* **2001**, *15*, 43.
(48) Ghorai, P.; Dussault, P. H. *Org. Lett.* **2009**, *11*, 213.
(49) Ghorai, P.; Dussault, P. H. *Org. Lett.* **2008**, *10*, 4577.
(50) Adam, W.; Mitchell, C. M. *Angew. Chem., Int. Ed.* **1996**, *35*, 533.

(51) Bernini, R.; Mincione, E.; Barontini, M.; Fabrizi, G.; Pasqualetti, M.; Tempesta, S. *Tetrahedron* **2006**, *62*, 7733.
(52) (a) Kennedy-Smith, J. J.; Nolin, K. A.; Gunterman, H. P.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 4056.
(53) Nolin, K. A.; Krumper, J. R.; Pluth, M. D.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 14684.
(54) Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 11939.
(55) Ison, E. A.; Trivedi, E. R.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 15374.
(56) Nolin, K. A.; Ahn, R. W.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 12462.
(57) Nolin, K. A.; Ahn, R. W.; Kobayashi, Y.; Kennedy-Smith, J. J.; Toste, F. D. *Chem.—Eur. J.* **2010**, *16*, 9555.
(58) Kuninobu, Y.; Takai, K. *Chem. Rev.* **2011**, *111*, 1938.
(59) Horino, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 2144.
(60) Kuninobu, Y.; Kawata, A.; Nishi, M.; Takata, H.; Takai, K. *Chem. Commun.* **2008**, 6360.
(61) Kuninobu, Y.; Nishina, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc.* **2008**, *130*, 14062.
(62) Hua, R.-H.; Jiang, J.-L. *Curr. Org. Synth.* **2007**, *4*, 151.
(63) Kuninobu, Y.; Matsuki, T.; Takai, K. *Org. Lett.* **2010**, *12*, 2948.
(64) Kuninobu, Y.; Tokunaga, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 202.
(65) Kuninobu, Y.; Nishina, Y.; Shoitho, M.; Takai, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2766.
(66) Kuninobu, Y.; Nishina, Y.; Nakagawa, C.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 12376.
(67) Kuninobu, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2005**, *127*, 13498.
(68) Takaya, H.; Ito, M.; Murahashi, S. I. *J. Am. Chem. Soc.* **2009**, *131*, 10824.
(69) Espenson, J. H. *Coord. Chem. Rev.* **2005**, *249*, 329.
(70) Owens, G. S.; Arias, J.; Abu-Omar, M. M. *Catal. Today* **2000**, *55*, 317.
(71) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417.
(72) Davies, H. M. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6422.
(73) Davies, H. M. L.; Long, M. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 3518.
(74) Reddy, R. P.; Davies, H. M. L. *Org. Lett.* **2006**, *8*, 5013.