DOI: 10.1002/ejoc.201301140

Rhenium-Catalyzed Oxidative Cyanation of Tertiary Amines with TMSCN

Aijun Lin,[a] Hao Peng,[a] Ablimit Abdukader,[a] and Chengjian Zhu*[a,b]

Keywords: Synthetic methods / Cyanation / C–H activation / Rhenium / Amines

Oxidative cyanation of sp^3 C–H bonds at the α position of tertiary amines by using TMSCN as the cyanide donor and a novel high-valent rhenium(V) complex was developed. The reaction offers the corresponding α-aminonitriles in good yields with *tert*-butyl hydroperoxide as the oxidant under mild and acid-free reaction conditions.

Introduction

The invention of efficient and selective chemical methods for C–H bond functionalization is currently an important field in reaction design.[1] The direct utilization of C–H bonds offers a number of advantages from both environmental and economical viewpoints as prefunctionalization of the substrates is not required and the synthetic procedures are generally shorter. Transition-metal-catalyzed C–H bond activation, especially that of unactivated sp^3 C–H bonds, has emerged as an important method, but it remains a challenge in organic synthesis.[2,3] Recently, the direct oxidative cyanation of C–H bonds adjacent to nitrogen atoms has attracted much interest, as bifunctional organic compounds with adjacent functional groups are highly useful and versatile intermediates in organic synthesis; moreover, these compounds have been widely used in the construction of biologically active natural products, such as alkaloids and vicinal diamines.[4] Several examples of metal-based catalysts, such as Ru,[5] Fe,[6] V,[7] and Mo,[8] in the presence of oxidants for the direct oxidative cyanation of tertiary amines have been reported. We have also documented the gold(III)-catalyzed oxidative α-cyanation of sp^3 C–H bonds of tertiary amines with trimethylsilyl cyanide (TMSCN) as the cyanide donor, and the corresponding α-aminonitriles were obtained in good to excellent yields.[9]

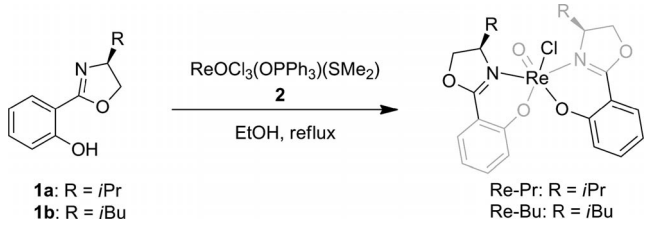
Homogeneous rhenium catalysis owing to its particular reactivity, chemoselectivity, functional group compatibility, and stability has attracted the attention of chemists in the past few years. Kuninobu and Takai reported low-valent rhenium(I)-based complexes for direct sp^2 C–H bond activation and subsequent C–C bond formation.[10] Very recently, Wang developed the first redox-neutral [4+2] annulation of benzamides and alkynes through C–H/N–H functionalization for rapid access to 3,4-dihydroisoquinolinones also on the basis of low-valent rhenium(I) catalysis.[11] The low-valent-rhenium-catalyzed regio- and stereoselective addition of imines and indoles to terminal alkynes through new C–C bond formation was independently reported by Fukumoto[12] and Wang.[13] High-valent rhenium catalysis, such as methyltrioxorhenium, was used as an efficient oxidation transformation catalyst;[14] however, the sparse availability and expensive nature of this reagent limited its wide application in organic synthesis. Recent work has indicated that high-valent rhenium bearing different types of ligands can be applied in different organic reactions. Toste and Abu-Omar et al. designed and synthesized a variety of high-valent rhenium oxo and imido complexes that have shown efficient activities in catalytic reduction reactions.[15] To the best of our knowledge, there have been few reports on C–H activation, especially sp^3 C–H bond activation, under the catalysis of high-valent, low toxicity, and air-stable rhenium complexes.[16] With our continuous interest in rhenium catalysis[17] and sp^3 C–H bond activation,[18] we herein present our results on the oxidative cyanation of sp^3 C–H bonds at the α position of tertiary amines in the presence of a novel stable oxorhenium(V) complex catalyst (Re-Bu). This method affords a facile approach to the synthesis of α-aminonitriles under solvent-free and acid-free reaction conditions.

Results and Discussion

The strategy for the preparation of high-valent rhenium complexes Re-Pr and Re-Bu is shown in Scheme 1. Reaction of readily available oxazoline ligands **1**[19] with Re^V-oxo dimethyl sulfide complex **2** in EtOH under reflux conditions resulted in a bright green solid that could be separated by filtration and thoroughly washed with cold ether and ethanol.[20] Slow evaporation of a solution of the Re-Bu complex offered X-ray-quality acicular crystals in high yield

[a] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China
E-mail: cjzhu@nju.edu.cn
http://hysz.nju.edu.cn/cjzhu/
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 345 Lingling Road, Shanghai 200032, P. R. China
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201301140.

at room temperature.[21] The ORTEP diagram of the Re-Bu complex is shown in Figure 1. The Re-Bu complex possesses distorted octahedral geometry, in which the terminal double-bonded oxygen atom is *trans* to the oxygen atom of one oxazoline ligand, and the chloride atom is *trans* to the oxygen atom of the another oxazoline ligand. The length of the Re=O bond is 1.718(6) Å, which is within the normal range of double-bonded rhenium oxo complexes.[22]



Scheme 1. Synthesis of oxorhenium oxazoline complexes Re-Pr and Re-Bu.

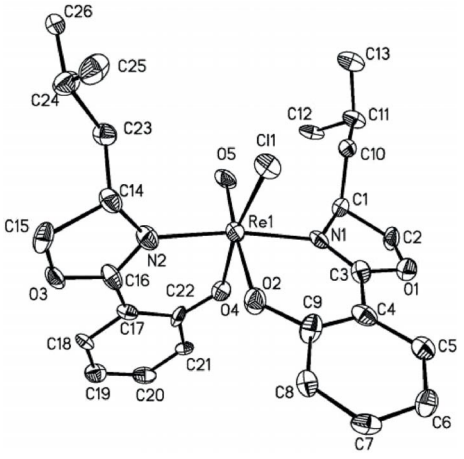
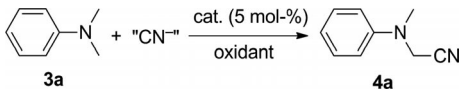


Figure 1. ORTEP molecular structure representation of Re-Bu.

Initial studies on the catalytic activities of the high-valent oxorhenium(V) oxazoline complexes Re-Pr and Re-Bu were performed to explore their potential in the oxidative cyanation reactions of tertiary amines. *N*,*N*-Dimethylaniline **3** was chosen as the model substrate to optimize the reaction conditions with various rhenium complex catalysts, oxidants, and cyanide sources at room temperature (Table 1). In the presence of Re-Pr (5 mol-%), corresponding aminonitrile **4a** was obtained in 78% yield with trimethylsilyl cyanide (TMSCN) as the cyanide source and *tert*-butyl hydroperoxide (TBHP, 5–6 M in decane) as the oxidant. To our delight, upon testing Re-Bu, the yield of **4a** improved to 86% (Table 1, entry 2). Perrhennate salts ($KReO_4$ and NH_4ReO_4) offered **4a** in low yield (Table 1, entries 3 and 4). Other monooxorhenium or dioxorhenium compounds offered **4a** in moderate yield (Table 1, entries 5–8). A high temperature was detrimental to the oxidative cyanation reaction owing to the generation of more oxidative byproducts such as *N*-methyl-*N*-phenylformamide (Table 1, entry 9). Moreover, upon testing different oxidants with the use of Re-Bu as the catalyst, TBHP proved to be the most suitable oxidant (Table 1, entry 2 vs. entries 10–13). Relative to $K_3[Fe(CN)_6]$, $CH_2(CN)_2$, and CH_3CN, TMSCN was the best cyanide source (Table 1, entry 2 vs. entries 14–16). $CH_2(CN)_2$ afford **4a** in 42% yield, which can be attributed to oxidative degradation of malononitrile through cleavage of the C–CN bond by the rhenium complex.[23] Further studies indicated that reducing the catalyst loading to 3 and 1 mol-% clearly affected the catalytic efficiency (Table 1, entries 17 and 18).

Table 1. Optimization of the reaction conditions.[a]



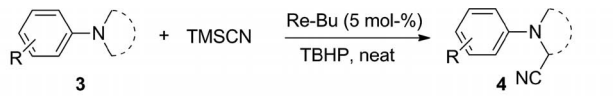
Entry	Cat.	Oxidant	"CN–"	Yield[b] [%]
1	Re-Pr	TBHP	TMSCN	78
2	Re-Bu	TBHP	TMSCN	86
3	$KReO_4$	TBHP	TMSCN	8
4	NH_4ReO_4	TBHP	TMSCN	7
5	$[nBu_4N][ReOCl_4]$	TBHP	TMSCN	38
6	$ReOCl_2(OPPh_3)(SMe_2)$	TBHP	TMSCN	43
7	$ReOI_2(OEt)(PPh_3)_2$	TBHP	TMSCN	29
8	$ReO_2I(PPh_3)_2$	TBHP	TMSCN	56
9	Re-Bu	TBHP	TMSCN	45[c]
10	Re-Bu	CH_3CO_3tBu	TMSCN	<5
11	Re-Bu	$PhCO_3tBu$	TMSCN	n.r.
12	Re-Bu	*m*CPBA[d]	TMSCN	<5
13	Re-Bu	O_2	TMSCN	n.r.
14	Re-Bu	TBHP	$K_3[Fe(CN)_6]$	n.r.
15	Re-Bu	TBHP	$CH_2(CN)_2$	42
16	Re-Bu	TBHP	CH_3CN	n.r.
17	Re-Bu	TBHP	TMSCN	71[e]
18	Re-Bu	TBHP	TMSCN	47[f]

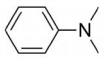
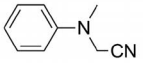
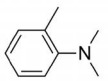
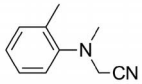
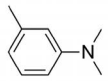
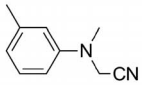
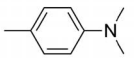
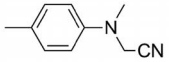
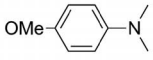
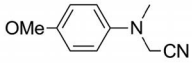
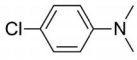
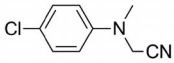
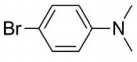
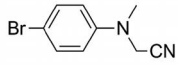
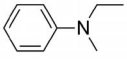
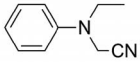
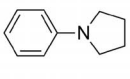
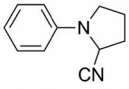
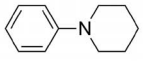
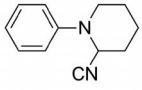
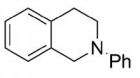
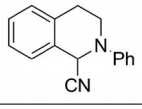
[a] All reactions were performed with **3** (0.5 mmol), cyanide (1.2 equiv.), and oxidant (2.5 equiv.). [b] Yield of isolated product; n.r.: no reaction. [c] The temperature was 60 °C. [d] *m*CPBA = *meta*-chloroperoxybenzoic acid. [e] 3 mol-% catalyst was used. [f] 1 mol-% catalyst was used.

With the optimal conditions for the highly selective oxidative cyanation of tertiary amines in hand, the scope of the reaction was investigated by using TMSCN as the cyanide source, TBHP as the oxidant, and Re-Bu (5 mol-%) as the catalyst at room temperature. As shown in Table 2, substituted *N*,*N*-dimethylanilines with electron-donating and electron-withdrawing groups were selectively and efficiently converted into the corresponding α-aminonitriles in good yields (Table 2, entries 2–7). *N*,*N*-Dimethyl-*o*-toluidine offered a slightly lower yield (70% yield) than both *N*,*N*-dimethyl-*m*-toluidine (78% yield) and *N*,*N*-dimethyl-*p*-toluidine (82% yield) owing to steric hindrance. Upon using *N*-methyl-*N*-ethylaniline as the substrate, the *N*-methyl group was oxidized chemoselectively to offer the corresponding *N*-ethyl-*N*-phenylaminoacetonitrile in 72% yield (Table 2, entry 8). This system was also applied efficiently to cyclic amines: piperidine, pyrrolidine, and tetrahydroisoquinoline derivatives were all converted into the corresponding α-cyanoamines in good yields (Table 2, entries 9–11). Unluckily, products **4i**–**k** were isolated without any enantioselectivities. Primary and secondary amines such as

benzylamine and dibenzylamine were tested under the optimal reaction conditions, but the corresponding products were not obtained. To demonstrate the practical utility of this method, scale-up experiments were performed with 10.0 mmol of *N*,*N*-dimethylaniline, and **4a** was obtained in 83% yield (1.21 g).

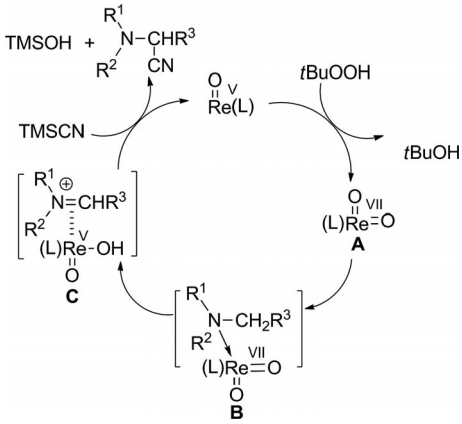
Table 2. Re-Bu complex catalyzed oxidative cyanation of *N*,*N*-dialkylanilines.[a]



Entry	Substrate	Product		Yield[b] [%]
1			**4a**	83 [c]
2			**4b**	70
3			**4c**	78
4			**4d**	82
5			**4e**	80
6			**4f**	77
7			**4g**	75
8			**4h**	72
9			**4i**	67
10			**4j**	81
11			**4k**	74

[a] All reactions were performed with the tertiary amine (0.5 mmol), TMSCN (1.2 equiv.), and TBHP (2.5 equiv.). [b] Yield of isolated product. [c] Tertiary amine (10.0 mmol).

A probable mechanism for the oxidative cyanation of the sp^3 C–H bonds of tertiary amines catalyzed by the Re-Bu complex is showed in Scheme 2. With an excess amount of TBHP as the oxidant, the oxorhenium(V) complex readily affords dioxorhenium(VII) product **A**, which further combines with *N*,*N*-dimethylaniline to form intermediate complex **B**. Intermediate **B** produces iminium ion transition state **C** through electron transfer from the α-carbon-centered radical and subsequent hydrogen transfer. Then, nucleophilic attack **C** gives the corresponding α-cyanated product and regenerates the oxorhenium(V) complex to complete the catalytic cycle.



Scheme 2. The proposed reaction mechanism for the high-valent rhenium complex catalyzed oxidative cyanation of tertiary amines.

Conclusions

In summary, we have described a novel high-valent rhenium complex catalyzed oxidative cyanation reaction of tertiary amines with trimethylsilyl cyanide and TBHP under acid-free conditions at room temperature for the first time. The reaction proceeds with high efficiency to give the corresponding α-cyanated amines, which are extremely useful synthetic intermediates in the construction of biologically important compounds. Further studies concerning the mechanistic details and asymmetric catalysis are now in progress in our laboratory.

Experimental Section

Typical Procedure for the Synthesis of Oxazoline Ligands: An amino alcohol (5 mmol) was added to a solution of 2-hydroxybenzonitrile (0.69 g, 5 mmol) and triphenylphosphine (4.8 g, 18.3 mmol) in CH_3CN (40 mL) under an atmosphere of argon at room temperature. To the resulting white suspension was added triethylamine (3.1 mL, 44.2 mmol) with stirring, and a clear colorless solution was obtained. CCl_4 (9.9 mL, 100.0 mmol) was added dropwise to the reaction mixture over 4 h. During the course of the addition of the CCl_4, a precipitate formed and the reaction mixture changed color to dark red. The reaction was stirred for a further 48 h, which resulted in a dark red suspension. The solution was then filtered, and the colorless residue was washed with diethyl ether (2×30 mL). The filtrate and washing were combined, the resulting precipitate was removed by filtration, and the process was repeated until no more solids precipitated. The filtrate was removed under reduced pressure to leave a sticky, dark red-brown residue, which was extracted into hexane (200 mL). The solvent was evaporated under reduced pressure to give a viscous, colorless residue. The residue was purified by column chromatography (SiO_2; hexane/ethyl acetate, 50:1). The corresponding oxazoline was obtained as a colorless oil.[19]

1a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.0 (s, 1 H), 7.65–7.62 (m, 1 H), 7.38–7.34 (m, 1 H), 7.02–6.98 (m, 1 H), 6.87–6.84 (m,1 H),

4.42–4.39 (m, 1 H), 4.13–4.09 (m, 1 H), 4.08–4.05 (m, 1 H), 1.80–1.75 (m, 1 H), 1.03–1.00 (m, 3 H), 0.98–0.90 (m, 3 H) ppm.

1b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.4 (s, 1 H), 7.67–7.61 (m, 1 H), 7.40–7.37 (m, 1 H), 7.02–6.99 (m, 1 H), 6.87–6.85 (m, 1 H), 4.47–4.45 (m, 2 H), 3.95- 3.92 (m, 1 H), 1.92–1.89 (m, 1 H), 1.67–1.65 (m, 1 H), 1.42–1.40 (m, 2 H), 1.02–0.99 (m, 3 H), 0.97–0.95 (m, 3 H) ppm.

Typical Procedure for the Synthesis of Oxorhenium Oxazoline Complexes: Ligand **1a** or **1b** (1 mmol) was dissolved in ethanol (50 mL), followed by 2,6-lutidene (0.29 mL, 1 mmol). $ReOCl_2(OPPh_3)(SMe_2)$ (299 mg, 0.46 mmol) was added to the flask within 5 min. The solution was heated at reflux under an atmosphere of argon for 4 h, cooled to room temperature, and filtered to yield a green solid, which was washed with cold ether (3 × 10 mL) and then dried.[20]

Re-Pr: Dark green powder (223 mg, 75%); m.p. 251 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J = 7.5 Hz, 1 H), 7.73 (d, J = 7.5 Hz, 1 H), 7.46–7.40 (m, 1 H), 7.26–7.21 (m, 1 H), 6.97–6.92 (m, 1 H), 6.85–6.72 (m, 3 H), 5.17–5.14 (m, 1 H), 4.91–4.87 (m, 2 H), 4.69–4.67 (m, 1 H), 4.60–4.57 (m, 1 H), 4.45–4.39 (m, 1 H), 2.98–2.86 (m, 2 H), 1.10–1.05 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.8, 171.4, 168.4, 164.5, 136.5, 130.8, 121.7, 119.5, 118.3, 110.1, 109.1, 76.3, 69.6, 67.9, 29.0, 19.3, 18.5, 15.1, 14.1 ppm. HRMS (ESI): calcd. for $[C_{24}H_{28}N_2O_5Re]^+$ 609.1526; found 609.1523.

Re-Bu: Bright green powder (254 mg, 82%); m.p. 265 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 1 H), 7.65 (d, J = 1.5 Hz, 1 H), 7.27–7.22 (m, 1 H), 7.07–7.04 (m, 1 H), 6.89–6.86 (m, 1 H), 6.68–6.58 (m, 3 H), 5.51–5.49 (m, 1 H), 4.95–4.91 (m, 2 H), 4.80–4.78 (m, 1 H), 4.64–4.59 (m, 1 H), 4.48–4.46 (m, 1 H), 2.63–2.54 (m, 2 H), 1.84–1.40 (m, 2 H) 1.10–0.92 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.1, 171.4, 167.9, 164.5, 136.0, 130.9, 130.2, 122.3, 121.8, 118.7, 117.4, 109.9, 109.4, 73.8, 69.4, 68.1, 43.8, 42.7, 41.8, 25.6, 23.9, 21.9, 21.5, 21.2 ppm. HRMS (ESI): calcd. for $[C_{26}H_{32}N_2O_5Re]^+$, 637.1846; found 637.1835.

Typical Procedure for the Oxidative Cyanation of Tertiary Amines Catalyzed by Re-Bu: A mixture of the amine (0.5 mmol), trimethylsilyl cyanide (0.6 mmol), Re-Bu (5 mol-%), and TBHP (5–6 M in decane, 1.25 mmol) was stirred at room temperature for 5 h. At the end of the reaction, as monitored by TLC, the reaction was quenched by the addition of a saturated solution of $NaHCO_3$ (2 mL), and the mixture was extracted with ethyl acetate (3–5 mL). The combined organic layer was washed with brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel. The fraction was collected and concentrated to give the desired product.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR and ^{13}C NMR spectra, mass spectra, and crystallographic details.

Acknowledgments

The authors gratefully acknowledge the National Natural Science Foundation of China (NSFC) (grant numbers 21172106, 21074054), the National Basic Research Program of China (grant number 2010CB923303), and the Research Fund for the Doctoral Program of Higher Education of China (grant number 20120091110010) for their financial support.

[1] For selected reviews on C–H functionalization, see: a) J.-Q. Yu, Z.-J. Shi, *C–H Activation*, Springer, Berlin, **2010**; b) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196–5217; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115; c) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655; d) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931; e) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315–1345; f) J. Wencel-Delord, T. Droge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740–4761; g) T. Bruckl, R. D. Baxter, Y. Ishihara, P. S. Baran, *Acc. Chem. Res.* **2012**, *45*, 826–839; h) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879–5918; i) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788–802; j) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2012**, *45*, 814–825; k) S. R. Neufeldt, M. S. Sanford, *Acc. Chem. Res.* **2012**, *45*, 936–946; l) L. G. Mercier, M. Leclerc, *Acc. Chem. Res.* **2013**, *46*, 1597–1605; m) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369–375.

[2] For selected reviews on C(sp^3)–H functionalization, see: a) R. H. Crabtree, *J. Organomet. Chem.* **2004**, *689*, 4083–4091; b) K. R. Campos, *Chem. Soc. Rev.* **2007**, *36*, 1069–1084; c) R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654–2672; d) J. F. Hartwig, *Chem. Soc. Rev.* **2011**, *40*, 1992–2002; e) H. Li, B.-J. Li, Z.-J. Shi, *Catal. Sci. Technol.* **2011**, *1*, 191–206; f) T. A. Ramirez, B. G. Zhao, Y. Shi, *Chem. Soc. Rev.* **2012**, *41*, 931–942; g) O. Baudoin, *Chem. Soc. Rev.* **2011**, *40*, 4902–4911.

[3] For selected reviews on C(sp^3)–H functionalization in organic Synthesis see: a) K. Godula, D. Sames, *Science* **2006**, *312*, 67–72; b) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417–424; c) W. R. Gutekunst, P. S. Baran, *Chem. Soc. Rev.* **2011**, *40*, 1976–1991; for selected examples of catalytic C(sp^3)–H functionalization in the syntheses of complex molecules, see: d) H. M. L. Davies, X. Dai, M. S. Long, *J. Am. Chem. Soc.* **2006**, *128*, 2485–2490; e) E. M. Stang, M. C. White, *Nat. Chem.* **2009**, *1*, 547–551; f) M. Chaumontet, R. Piccardi, O. Baudoin, *Angew. Chem.* **2009**, *121*, 185–188; *Angew. Chem. Int. Ed.* **2009**, *48*, 179–182; g) Y. Feng, G. Chen, *Angew. Chem.* **2010**, *122*, 970–973; *Angew. Chem. Int. Ed.* **2010**, *49*, 958–961; h) W. R. Gutekunst, P. S. Baran, *J. Am. Chem. Soc.* **2011**, *133*, 19076–19079.

[4] a) D. Lucet, T. Le Gall, C. Mioskowski, *Angew. Chem.* **1998**, *110*, 2724–2772; *Angew. Chem. Int. Ed.* **1998**, *37*, 2580–2627; b) D. Enders, J. P. Shilvock, *Chem. Soc. Rev.* **2000**, *29*, 359–373.

[5] a) S.-I. Murahashi, N. Komiya, H. Terai, T. Nakae, *J. Am. Chem. Soc.* **2003**, *125*, 15312–15313; b) M. North, *Angew. Chem.* **2004**, *116*, 4218–4220; *Angew. Chem. Int. Ed.* **2004**, *43*, 4126–4128; c) S.-I. Murahashi, N. Komiya, H. Terai, *Angew. Chem.* **2005**, *117*, 7091–7093; *Angew. Chem. Int. Ed.* **2005**, *44*, 6931–6933; d) S.-I. Murahashi, D. Zhang, *Chem. Soc. Rev.* **2008**, *37*, 1490–1501; e) S. Verma, S. L. Jain, B. Sain, *Catal. Lett.* **2011**, *141*, 882–885.

[6] a) W. Han, A. R. Ofial, *Chem. Commun.* **2009**, 5024–5026; b) P. Liu, Y. G. Liu, E. L.-M. Wong, S. Xiang, C.-M. Che, *Chem. Sci.* **2011**, *2*, 2187–2195.

[7] S. Singhal, S. L. Jain, B. Sain, *Chem. Commun.* **2009**, 2371–2372.

[8] K. Alagiri, K. R. Prabhu, *Org. Biomol. Chem.* **2012**, *10*, 835–842.

[9] Y. Zhang, H. Peng, M. Zhang, Y.-X. Cheng, C.-J. Zhu, *Chem. Commun.* **2011**, *47*, 2354–2356.

[10] a) Y. Kuninobu, Y. Nishina, M. Shouho, K. Takai, *Angew. Chem.* **2006**, *118*, 2832–2834; *Angew. Chem. Int. Ed.* **2006**, *45*, 2766–000; b) Y. Kuninobu, A. Kawata, K. Takai, *J. Am. Chem. Soc.* **2005**, *127*, 13498–13499; c) Y. Horino, *Angew. Chem.* **2007**, *119*, 2192–2194; *Angew. Chem. Int. Ed.* **2007**, *46*, 2144–2146; d) Y. Kuninobu, Y. Nishina, T. Matsuki, K. Takai, *J. Am. Chem. Soc.* **2008**, *130*, 14062–14063; e) Y. Kuninobu, A. Ka-

wata, M. Nishi, H. Takata, K. Takai, *Chem. Commun.* **2008**, 6360–6362; f) Y. Kuninobu, K. Takai, *Chem. Rev.* **2011**, *111*, 1938–1953.

[11] Q. Tang, D. Xia, X. Jin, Q. Zhang, X. Sun, C. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 4628–4631.

[12] Y. Fukumoto, M. Daijo, N. Chatani, *J. Am. Chem. Soc.* **2012**, *134*, 8762–8765.

[13] D. Xia, Y. Wang, Z. Du, Q. Zheng, C. Wang, *Org. Lett.* **2012**, *14*, 588–591.

[14] a) F. E. Kühn, A. M. Santos, I. S. Gonçalves, C. C. Romão, A. D. Lopes, *Appl. Organomet. Chem.* **2001**, *15*, 43–50; b) P. Ghorai, P. H. Dussault, *Org. Lett.* **2009**, *11*, 213–216; c) P. Ghorai, P. H. Dussault, *Org. Lett.* **2008**, *10*, 4577–4579; d) W. Adam, C. M. Mitchell, *Angew. Chem.* **1996**, *108*, 578–581; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 533–535; e) R. Bernini, E. Mincione, M. Barontini, G. Fabrizi, M. Pasqualetti, S. Tempesta, *Tetrahedron* **2006**, *62*, 7733–7737.

[15] a) J. J. Kennedy-Smith, K. A. Nolin, H. P. Gunterman, F. D. Toste, *J. Am. Chem. Soc.* **2003**, *125*, 4056–4057; b) K. A. Nolin, J. R. Krumper, M. D. Pluth, R. G. Bergman, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 14684–14696; c) E. A. Ison, R. A. Corbin, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2005**, *127*, 11938–11939; d) E. A. Ison, E. R. Trivedi, R. A. Corbin, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2005**, *127*, 15374–15375; e) K. A. Nolin, R. W. Ahn, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 12462–12463; f) K. A. Nolin, R. W. Ahn, Y. Kobayashi, J. J. Kennedy-Smith, F. D. Toste, *Chem. Eur. J.* **2010**, *16*, 9555–9562.

[16] H. Takaya, M. Ito, S. I. Murahashi, *J. Am. Chem. Soc.* **2009**, *131*, 10824–10825.

[17] H. Peng, A. J. Lin, Y. Zhang, H. L. Jiang, J. C. Zhou, Y. X. Cheng, C. J. Zhu, H. W. Hu, *ACS Catal.* **2012**, *2*, 163–167.

[18] a) J. Xie, H. M. Li, J. C. Zhou, Y. X. Cheng, C. J. Zhu, *Angew. Chem.* **2012**, *124*, 1278–1281; *Angew. Chem. Int. Ed.* **2012**, *51*, 1252–1255; b) J. Xie, H. L. Jiang, Y. X. Cheng, C. J. Zhu, *Chem. Commun.* **2012**, *48*, 979–981; c) J. Xie, H. M. Li, Q. C. Xue, Y. X. Cheng, C. J. Zhu, *Adv. Synth. Catal.* **2012**, *354*, 1646–1650; d) Q. C. Xue, J. Xie, H. M. Li, Y. X. Cheng, C. J. Zhu, *Chem. Commun.* **2013**, *49*, 3700–3702; e) Q. C. Xue, J. Xie, H. M. Jin, Y. X. Cheng, C. J. Zhu, *Org. Biomol. Chem.* **2013**, *11*, 1606–1609; f) J. Xie, Q. C. Xue, H. M. Jin, H. M. Li, Y. X. Cheng, C. J. Zhu, *Chem. Sci.* **2013**, *4*, 1281–1286.

[19] a) H. R. Hoveyda, V. Karunaratne, S. J. Rettig, C. Orvig, *Inorg. Chem.* **1992**, *31*, 5408–5416; b) D. Franco, M. Gómez, F. Jiménez, G. Muller, M. Rocamora, M. A. Maestro, J. Mahía, *Organometallics* **2004**, *23*, 3197–3209.

[20] J. Arias, C. R. Newlands, M. M. Abu-Omar, *Inorg. Chem.* **2001**, *40*, 2185–2192.

[21] CCDC-819089 (for Re-Bu) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] W. A. Herrmann, F. E. Kühn, *Acc. Chem. Res.* **1997**, *30*, 169–180.

[23] Z.-P. Li, C.-J. Li, *Eur. J. Org. Chem.* **2005**, 3173–3176.

Received: July 30, 2013
Published Online: October 9, 2013

