JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Mn-Catalyzed Aromatic C−H Alkenylation with Terminal Alkynes

Bingwei Zhou,[†] Hui Chen,*[,‡] and Congyang Wang*[,†]

[†]Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, [‡]CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

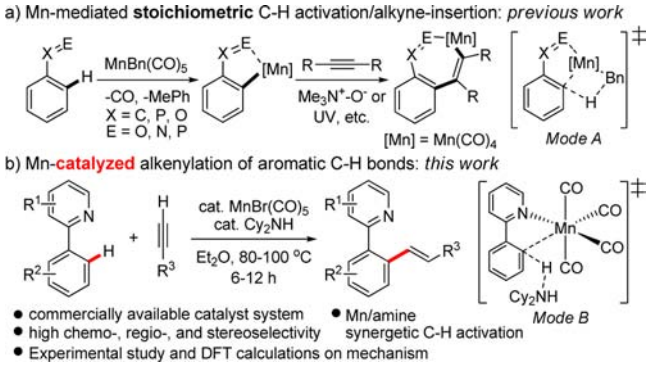
Supporting Information

ABSTRACT: The first *manganese-catalyzed* aromatic C−H alkenylation with terminal alkynes is described. The procedure features an operationally simple catalyst system containing commercially available $MnBr(CO)_5$ and dicyclohexylamine (Cy_2NH). The reaction occurs readily in a highly chemo-, regio-, and stereoselective manner delivering *anti*-Markovnikov *E*-configured olefins in high yields. Experimental study and DFT calculations reveal that (1) the reaction is initiated by a C−H activation step via the cooperation of manganese and base; (2) manganacycle and alkynylmanganese species are the key reaction intermediates; and (3) the ligand-to-ligand H-transfer and alkynyl-assisted C−H activation are the key steps rendering the reaction catalytic in manganese.

Recently, the direct functionalization of inert C—H bonds ubiquitous in organic molecules has attracted intensive attention since it holds great potential in reshaping traditional organic synthesis.[1] Second- and third-row transition metals, such as Pd, Rh, and Ru, are major players in this arena and have witnessed explosive success in catalytic C—C and C—X bond formation reactions.[2] In contrast, using the first-row transition metals for such catalytic transformations has been considerably less studied despite their high abundance in earth's crust, low cost, and promising reactivities.[3] For manganese in particular, although Bruce et al.[4] reported seminal work on stoichiometric *ortho*-manganation of benzylideneaniline as early as in 1971, there are only a few examples of Mn-catalyzed C—C bond formation reactions via inert C—H activation.[5−7] Kuninobu and Takai et al. elegantly demonstrated a Mn-catalyzed imidazole-directed addition of aromatic C—H bonds to the polar C═O bond of aldehydes.[5] Note that the presence of silanes plays a key role in making this reaction catalytic in Mn.

For the related addition to unpolarized C−C triple bonds of alkynes, however, only stoichiometric versions have been disclosed to date.[8] The groups of Liebeskind, Nicholson, Suárez, and others showed the formation of five-member manganacycles with a stoichiometric $MnBn(CO)_5$ reagent, which was prepared from stepwise reactions employing $Mn_2(CO)_{10}$, Na/Hg amalgam, and benzylchloride (Scheme 1a).[9] The ensuing insertion of alkynes into Mn−C_{aryl} bonds gave seven-member manganacycles upon heating, photoirradiation, or with the reagent of trimethylamine *N*-oxide.[8] Clearly, challenges still remain for the successful development of practical Mn-catalyzed C−H alkenylation reactions: (i) the avoidance of tedious syntheses and stoichiometric use of $MnR(CO)_5$ (R = Bn, Me, Ph) reagents; (ii) the ensuing need to develop new modes of C−H activation by Mn due to $MnR(CO)_5$ being indispensably employed for such stoichiometric reactions,[4,8] as it is generally accepted that the R group of $MnR(CO)_5$ serves as an intramolecular H-acceptor in the C−H activation step (Mode A); (iii) the transformation of seven-member manganacycles into alkenylated products and, more importantly, regenerating the catalytic species of manganese. With these concerns, we herein uncover a novel catalyst system containing commercially available $MnBr(CO)_5$ and dicyclohexylamine (Cy_2NH), which enables efficient aromatic C−H activation via Mn/amine cooperation (Mode B). Accordingly, we demonstrate the first Mn-catalyzed aromatic C−H alkenylations with terminal alkynes (Scheme 1b).[10] Of note, terminal alkynes are often nontrivial substrates in C−H alkenylation reactions due to their relatively acidic terminal protons and ease of self-di- or trimerizations in transition metal catalysis.[11]

Scheme 1. Mn-Promoted C−H Alkenylations with Alkynes



We commenced our reaction with arylpyridine **1g** and alkyne **2a** as model substrates (Table 1). No products were detected in toluene with mere $MnBr(CO)_5$ as a catalyst (entry 1). Surprisingly, the alkenylated product **3ga** was formed in 24% NMR yield when a catalytic amount of triethylamine (Et_3N), a weak base, was added into the reaction (entry 2). The screening of solvents revealed Et_2O as being optimal (entry 3).[12] An array of bases were then examined, and secondary amines bearing proper steric bulkiness were noted to be beneficial for the reaction (entries 4−6).[12] Inspired by the *N*-heterocyclic carbene (NHC) and pyridine ligands developed by Glorius[13a] and Yu[13b] respectively, we tested a series of secondary amines of varied carbocycle ring sizes ranging from **A-1** to **A-4**.[12] To our delight, largely enhanced yields of **3ga** were generally obtained with dicyclohexylamine (**A-2**) being the best (entries 7−10). Further

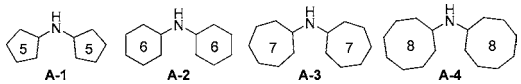
Received: November 30, 2012
Published: January 3, 2013

dx.doi.org/10.1021/ja311689k | J. Am. Chem. Soc. 2013, 135, 1264−1267

Table 1. Screening of Reaction Parameters[a]

entry	cat. (10 mol %)	base (20 mol %)	solvent	yield (%)[b]
1	$MnBr(CO)_5$	–[c]	toluene	0
2	$MnBr(CO)_5$	Et_3N	toluene	24
3	$MnBr(CO)_5$	Et_3N	Et_2O	34
4	$MnBr(CO)_5$	$EtN(i\text{-}Pr)_2$	Et_2O	23
5	$MnBr(CO)_5$	$(i\text{-}Pr)_2NH$	Et_2O	37
6	$MnBr(CO)_5$	pyrrolidine	Et_2O	19
7	$MnBr(CO)_5$	**A-1**	Et_2O	50
8	$MnBr(CO)_5$	**A-2**	Et_2O	57
9	$MnBr(CO)_5$	**A-3**	Et_2O	52
10	$MnBr(CO)_5$	**A-4**	Et_2O	54
11	$Mn_2(CO)_{10}$	**A-2**	Et_2O	58
12	$ReBr(CO)_5$	**A-2**	Et_2O	4
13	$Ru_3(CO)_{12}$	**A-2**	Et_2O	8
14	$Mn(acac)_3$	**A-2**	Et_2O	0
15[d]	*$MnBr(CO)_5$*	*A-2*	*Et_2O*	*77(58)*[e]

[a]Reaction conditions unless otherwise noted: **1g** (0.2 mmol), **2a** (0.2 mmol), catalyst (0.02 mmol), base (0.04 mmol), solvent (0.5 mL), 100 °C, 6 h. [b]Yields of **3ga** determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. [c]No base. [d]**1g**/**2a** = 2:1. [e]Isolated yield of **3ga** on 0.5 mmol scale with 0.5 mL of Et_2O; **3ga**/**6ga** = 17:1; 48% of **1g** was recovered after reaction.

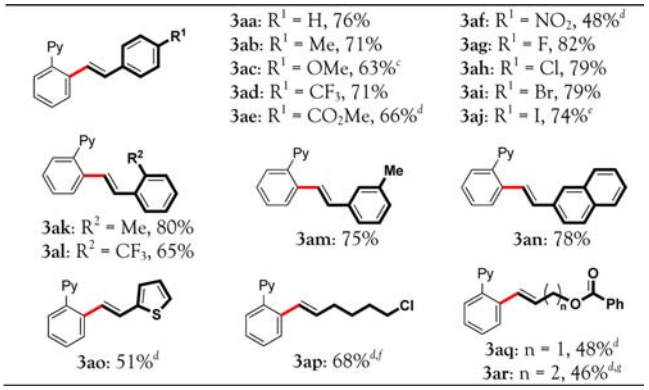


variations on metal catalysts showed that $Mn_2(CO)_{10}$ worked as well, while other metal carbonyls, such as $ReBr(CO)_5$ and $Ru_3(CO)_{12}$, and noncarbonyl manganese catalysts exhibited much lower activity, if any at all (entries 11–14).[12] Finally, the optimal reaction conditions were obtained by tuning the ratio of **1g**/**2a** (entry 15). It should be noted that only a small amount of Z-isomer **6ga** was detected (**3ga**/**6ga** = 17:1) and neither dialkenylated product **4ga** nor Markovnikov adduct **5ga** was observed in the reaction, which reflects a high level of chemo-, regio-, and stereocontrol in this protocol.

With the optimized conditions in hand, we next explored the scope of alkynes (Scheme 2). Both electro-donating and -withdrawing groups on aromatic alkynes are well tolerated affording the expected products (**3aa**–**f**) in good yields. It is noteworthy that halogen functionalities, in particular Br and I, remain intact after reaction, providing easy handles for further synthetic elaborations (**3ag**–**j**). *Ortho*- and *meta*-substituents on the benzene moiety show no obvious influence on the reaction outcome (**3ak**–**m**). 2-Ethynylnaphthalene containing an extended conjugated system gives the corresponding product **3an** as well. As an example of a heteroaromatic alkyne, 2-ethynylthiophene is also amenable to this protocol (**3ao**). Aliphatic alkynes with varied functionalities are compatible with the reaction conditions (**3ap**–**r**), albeit displaying relatively sluggish reactivities. Finally, no reaction took place with internal alkynes, which hints at the reaction mechanism.

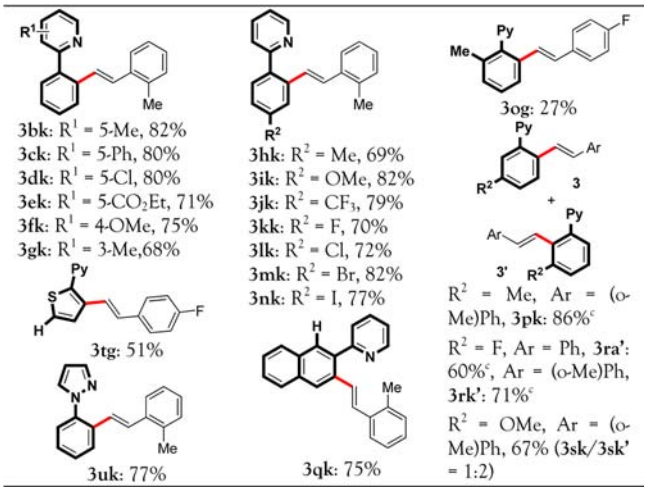
Next, a variety of arylpyridines were further examined (Scheme 3). Substituents on pyridine rings with disparate electronic properties have no obvious bias on the formation of products (**3bk**–**fk**). Arylpyridine **1g** bearing a 3-positioned methyl group gives rise to **3gk** smoothly despite the increased

Scheme 2. Scope of Alkynes[a,b]



[a]Reaction conditions: **1a** (1 mmol), **2** (0.5 mmol), $MnBr(CO)_5$ (0.05 mmol), Cy_2NH (0.1 mmol), Et_2O (1.2 mL), 80 °C, 6 h. [b] Isolated yields of product **3** are shown. [c] **3ac**/**6ac** = 9:1. [d] 100 °C, 12 h. [e] **3aj**/**6aj** = 9:1. [f] **3ap**/**5ap** = 9:1. [g] **3ar**/**5ar** = 8:1.

Scheme 3. Scope of Arylpyridines[a,b]



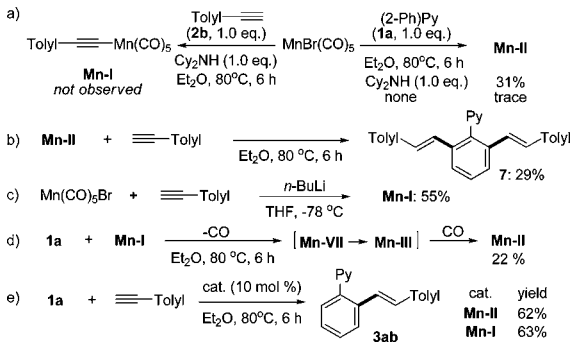
[a]Reaction conditions: **1** (1 mmol), **2** (0.5 mmol), $MnBr(CO)_5$ (0.05 mmol), Cy_2NH (0.1 mmol), Et_2O (1.2 mL), 80 °C, 6 h. [b] Isolated yields of **3** are shown. [c] Single product.

steric hindrance for C–H activation. Also, a wide array of functional groups on the benzene rings, again including fragile halogens, are compatible in the reaction despite their different electronic properties (**3hk**–**nk**). An *ortho*-substituent, however, has a profound influence on the reaction outcome (**3og**), which echoes the fact that no dialkenylated products are observed in the reaction for all cases. A perfect regioselectivity was found when two adjacent C–H bonds exist in the *meta*-substituted benzene moiety and single regioisomers of less steric bulkiness were obtained in high yields (**3pk**–**qk**). Interestingly, completely reversed regioselectivity was observed when a second-directing *m*-fluoro group exists affording **3ra**′ and **3rk**′ as the sole products. It proved that the *m*-methoxyl group had less directing effect resulting in the formation of a mixture of **3sk** and **3sk**′, which is consistent with Liebeskind's study.[8a] 2-Thiophenylpyridine was smoothly alkenylated on the 3-position of the thiophene ring though the C–H bond adjacent to the S-atom is often susceptible (**3tg**). 1-Phenylpyrazole is also amenable to this protocol affording **3uk** in good yield.

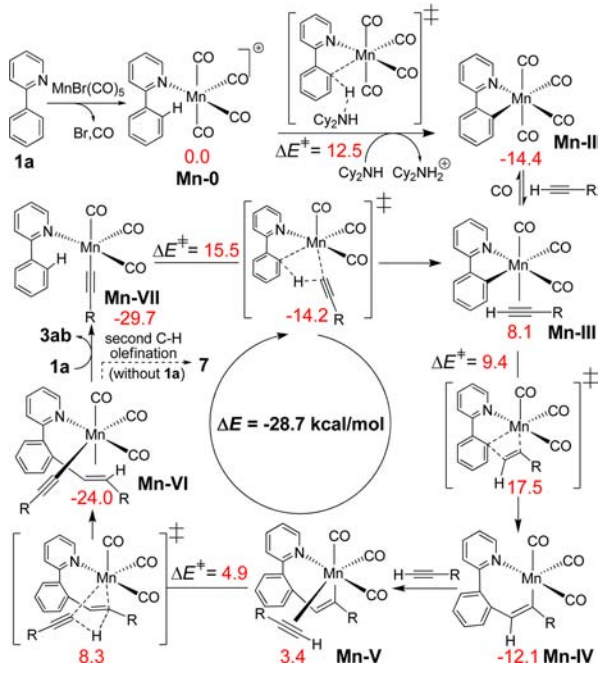
dx.doi.org/10.1021/ja311689k | J. Am. Chem. Soc. 2013, 135, 1264–1267

To probe the possible reaction mechanism, we conducted a series of experimental investigations. A stoichiometric reaction of $MnBr(CO)_5$ with alkyne **2b** was first examined in the presence of Cy_2NH (Scheme 4a, left). No alkynylmanganese species **Mn-I** was observed, which is in line with previous reports that the formation of **Mn-I** necessitated the existence of strong alkynyl nucleophiles or silver salts.[14] In contrast, $MnBr(CO)_5$ reacted with 2-phenylpyridine **1a** affording five-member manganacycle **Mn-II** (structure in Scheme 5) in 31% isolated yield (Scheme 4a, right). Remarkably, only a trace amount of **Mn-II** was detected in the absence of Cy_2NH, which underlies the key role of Cy_2NH in this C−H activation step. Subsequently, **Mn-II** was treated with alkyne **2b** and bis-olefin **7** was formed in 29% isolated yield (Scheme 4b). It is widely accepted[8] and confirmed by Nicholson[8g] and Suárez[8j] that seven-member manganacycles are formed by a regioselective insertion of alkyne into Mn−C_{aryl} bonds of five-member manganacycles. Therefore, we surmised that **Mn-IV** were formed from **Mn-II** and **2b** and would further react with **2b** to afford alkynylmanganese **Mn-VI** (Scheme 5).

Scheme 4. Mechanistic Experiments



Scheme 5. Proposed Reaction Mechanism with DFT Study[a]



[a]DFT computed relative energies and barriers (kcal/mol) with zero-point energy (ZPE) corrections are marked in red (for R = Ph).

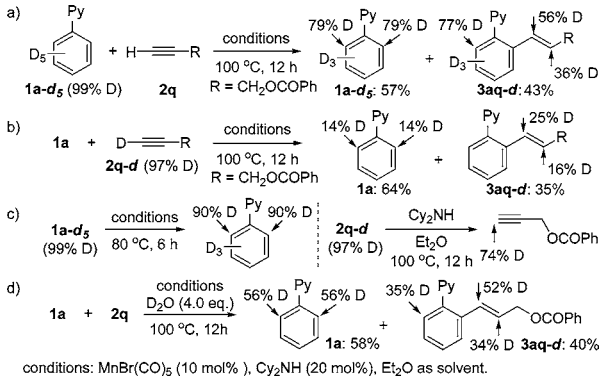
Note that a related alkynylmanganese species was found by Nicholson et al. as a byproduct in a stoichiometric reaction of *ortho*-manganated triphenylphosphate with phenylacetylene.[8g] The second C−H olefination of **Mn-VI** would finally lead to the formation of **7** in a stoichiometric reaction, while ligand exchange of **Mn-VI** with **1a** would deliver **Mn-VII** and release monoalkenylated product **3ab** in the catalytic reaction (Scheme 5). To further verify the involvement of **Mn-VII**, alkynylmanganese **Mn-I** was prepared from $MnBr(CO)_5$ and **2b** via a lithiation−trapping sequence (Scheme 4c).[14a] We envisioned that **Mn-I** and **1a** would undergo a ligand-exchange releasing CO to afford **Mn-VII**, which subsequently transforms into **Mn-III** via C−H activation, or further leads to **Mn-II** with recoordination of CO (Scheme 5). To our delight, **Mn-II** was isolated in 22% yield when **Mn-I** was treated with **1a** (Scheme 4d), which correlated with our hypothesis. Importantly, it was demonstrated that both **Mn-II** and **Mn-I** could catalyze the alkenylation of **1a** with **2b** affording **3ab** in comparable yields (Scheme 4e).

Based on these results, a plausible reaction mechanism is proposed in Scheme 5. Density functional theory (DFT) calculations were then conducted to shed light on the role of base in the initial C−H activation of 2-phenylpyridine **1a** and the profile of the whole catalytic cycle. First, it is seen from Scheme 5 that five-member manganacycle **Mn-II** can be easily generated from $[Mn(\mathbf{1a})(CO)_4]^+$ **Mn-0** with the aid of Cy_2NH base by an activation energy of 12.5 kcal/mol. This relatively low barrier is mainly due to the stability of **Mn-II**, which leads to an exothermic C−H activation process by 14.4 kcal/mol. This is in line with the experimental isolation of **Mn-II** as shown before. After replacement of one binding CO by an alkyne, **Mn-III** is reached as the starting point of the entire catalytic cycle. The subsequent insertion of alkyne into the Mn−C_{aryl} bond only needs to overcome a barrier of 9.4 kcal/mol, resulting in seven-member manganacycle **Mn-IV**. We speculate that the relatively crowded octahedron configuration of manganese in manganacycle **Mn-III** and **Mn-IV** accounts for the high chemo-, regio-, and stereoselectivity of this protocol. Then, **Mn-IV** reacts with another alkyne to protonate the alkenylmanganese group via a ligand-to-ligand H-transfer process and generates **Mn-VI** containing the final product, which is liberated from the catalytic cycle by substitution with **1a** affording alkynylmanganese **Mn-VII**. It can regenerate **Mn-III** via C−H activation assisted by the alkynyl ligand in **Mn-VII** with a barrier of 15.5 kcal/mol. Collectively, the whole catalytic cycle is exothermic by 28.7 kcal/mol.

To gain more details on the nature of Mn-catalyzed C−H activation, deuterium-labeling experiments were next explored. The reaction of pentadeuterated arylpyridine **1a**-d_5 and alkyne **2q** resulted in the incorporation of deuterium at both olefinic positions of **3aq**-*d* (Scheme 6a). Similarly, the scrambling of deuterium on the double bond of **3aq**-*d* was also observed when deuterated alkyne **2q**-*d* was treated with **1a** under the same conditions (Scheme 6b). These results are in good agreement with the reaction mechanism shown in Scheme 5. In addition, it was found that the sum of deuterium decreased after reactions and D/H were scrambled in the recovered starting materials (Scheme 6a,b), which raised the concern that D/H exchange might exist in the reaction. We therefore subjected mere **1a**-d_5 to the reaction, and the partial loss of deuterium was detected (Scheme 6c, left), indicating the C−H activation step might be a reversible deprotonation/protonation equilibrium. Also, the degree of deuteration in **2q**-*d* decreased upon treatment with base (Scheme 6c, right). Finally, the reaction of **1a** and **2q** in the

dx.doi.org/10.1021/ja311689k | J. Am. Chem. Soc. 2013, 135, 1264−1267

Scheme 6. Deuterium-Labeling Experiments



presence of external D_2O gave D-incorporated product **3aq-*d*** and the starting material **1a** further confirming the D/H exchange in the reaction (Scheme 6d).

In conclusion, the Mn-catalyzed C−H alkenylation with terminal alkynes was successfully developed for the first time. The reaction highlights not only a practical catalyst system consisting of commercially available $MnBr(CO)_5$ and Cy_2NH but also high levels of control in chemo-, regio-, and stereoselectivity. Experimental and computational investigations show that the reaction is initiated by a deprotonative C−H activation step via the synergy of manganese and base. Remarkably, key intermediates such as manganacycle and alkynylmanganese species were identified for the reaction. Moreover, the ligand-to-ligand H-transfer and alkynyl-assisted C−H activation steps are probed as key pathways to furnish the entire catalytic cycle. Further studies to explore Mn-catalyzed novel reactions using the combination of Mn catalysts and weak bases are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and computational procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

wangcy@iccas.ac.cn; chenh@iccas.ac.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Generous financial support from the Natural Science Foundation of China (21002103, 21290194), the Major State Basic Research Development Program (2012CB821600), and Institute of Chemistry, CAS are gratefully acknowledged.

■ REFERENCES

(1) Yu, J. Q.; Shi, Z. J. *C−H Activation*; Springer: Berlin, Germany, 2010.

(2) For recent leading reviews on C−H activation via the second- and third-row transition metal catalysis: (a) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788. (b) Hickman, A. J.; Sanford, M. S. *Nature* **2012**, *484*, 177. (c) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740. (d) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (e) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (f) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780. (g) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (h) Gutekunst, W. R.; Baran, P. S. *Chem. Soc. Rev.* **2011**, *40*, 1976. (i) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (j) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890. (k) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (l) Satoh, T.; Miura, M. *Chem.—Eur. J.* **2010**, *16*, 11212. (m) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Commun.* **2010**, *46*, 677. (n) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (o) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074.

(3) For leading reviews on C−H activation via the first-row transition metal catalysis: (a) White, M. C. *Science* **2012**, *335*, 807. (b) Zhang, C.; Tang, C.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3464. (c) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293. (d) Wendlandt, A. E.; Suess, A. M.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2011**, *50*, 11062. (e) Yoshikai, N. *Synlett* **2011**, *8*, 1047. (f) Nakamura, E.; Yoshikai, N. *J. Org. Chem.* **2010**, *75*, 6061. (g) Li, C.-J. *Acc. Chem. Res.* **2009**, *42*, 335. (h) Kulkarni, A. A.; Daugulis, O. *Synthesis* **2009**, 4087.

(4) (a) Bruce, M. I.; Goodall, B. L.; Iqbal, M. Z.; Stone, F. G. A. *Chem. Commun.* **1971**, 1595. (b) For a review on stoichiometric cyclomanganation, see: Albrecht, M. *Chem. Rev.* **2010**, *110*, 576.

(5) For inert $C(sp^2)$−H activation, see: (a) Kuninobu, Y.; Nishina, Y.; Takeuchi, T.; Takai, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6518. For one substrate with an olefinic C−H bond, see: (b) Kuninobu, Y.; Fujii, Y.; Matsuki, T.; Nishina, Y.; Takai, K. *Org. Lett.* **2009**, *11*, 2711.

(6) For activated C(sp)−H or $C(sp^3)$−H functionalization, see: (a) Kuninobu, Y.; Kawata, A.; Nishi, M.; Takata, H.; Takai, K. *Chem. Commun.* **2008**, 6360. (b) Kuninobu, Y.; Nishi, M.; Yudha, S. S.; Takai, K. *Org. Lett.* **2008**, *10*, 3009. (c) Kuninobu, Y.; Kikuchi, K.; Takai, K. *Chem. Lett.* **2008**, *37*, 740. (d) Tsuji, H.; Yamagata, K.-i.; Fujimoto, T.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 7792. (e) Yoshikai, N.; Zhang, S.; Yamagata, K.; Tsuji, H.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 4099. (f) Kuninobu, Y.; Kawata, A.; Nishi, M.; Yudha, S. S.; Chen, J.-J.; Takai, K. *Chem.—Asian J.* **2009**, *4*, 1424.

(7) For manganese-catalyzed C−X (X = heteroatom) bond formations, see: (a) Gunay, A.; Theopold, K. H. *Chem. Rev.* **2010**, *110*, 1060. (b) Borovik, A. S. *Chem. Soc. Rev.* **2011**, *40*, 1870.

(8) (a) Liebeskind, L.; Gasdaska, J. R.; McCallum, J. S.; Tremont, S. J. *J. Org. Chem.* **1989**, *54*, 669. (b) Robinson, N. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1989**, *364*, C37. (c) Cambie, R. C.; Metzler, M. R.; Rutledge, P. S.; Woodgate, P. D. *J. Organomet. Chem.* **1990**, *381*, C26. (d) Cambie, R. C.; Metzler, M. R.; Rutledge, P. S.; Woodgate, P. D. *J. Organomet. Chem.* **1990**, *398*, C22. (e) Grigsby, W. J.; Main, L.; Nicholson, B. K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 649. (f) Cambie, R. C.; Metzler, M. R.; Rutledge, P. S.; Woodgate, P. D. *J. Organomet. Chem.* **1992**, *429*, 41. (g) Grigsby, W. J.; Main, L.; Nicholson, B. K. *Organometallics* **1993**, *12*, 397. (h) Depree, G. J.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1998**, *551*, 281. (i) Tully, W.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **2001**, *633*, 162. (j) Suárez, A.; Faraldo, F.; Vila, J. M.; Adams, H.; Fernández, A.; López-Torres, M.; Fernández, J. J. *J. Organomet. Chem.* **2002**, *656*, 270. These stoichiometric reactions can be applied to the syntheses of indenols when carbonyls serve as directing groups; see refs 8a−d.

(9) Bruce, M. I.; Liddell, M. J.; Pain, G. N. *Inorg. Synth.* **1989**, *26*, 171.

(10) (a) Matsuura, Y.; Tamura, M.; Kochi, T.; Sato, M.; Chatani, N.; Kakiuchi, F. *J. Am. Chem. Soc.* **2007**, *129*, 9858. (b) Cheng, K.; Yao, B.; Zhao, J.; Zhang, Y. *Org. Lett.* **2008**, *10*, 5309.

(11) For dimerizations, see: (a) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067. (b) Jahier, C.; Zatolochnaya, O. V.; Zvyagintsev, N. V.; Ananikov, V. P.; Gevorgyan, V. *Org. Lett.* **2012**, *14*, 2846 and references therein. For trimerizations, see: (c) Domínguez, G.; Pérez-Castells, J. *Chem. Soc. Rev.* **2011**, *40*, 3430.

(12) For more details, see Supporting Information.

(13) (a) Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523. (b) Zhang, Y.-H.; Shi, B.-F.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 5072.

(14) (a) Sato, M.; Mogi, E. *J. Organomet. Chem.* **1996**, *517*, 1. (b) Miguel, D.; Riera, V. *J. Organomet. Chem.* **1985**, *293*, 379.