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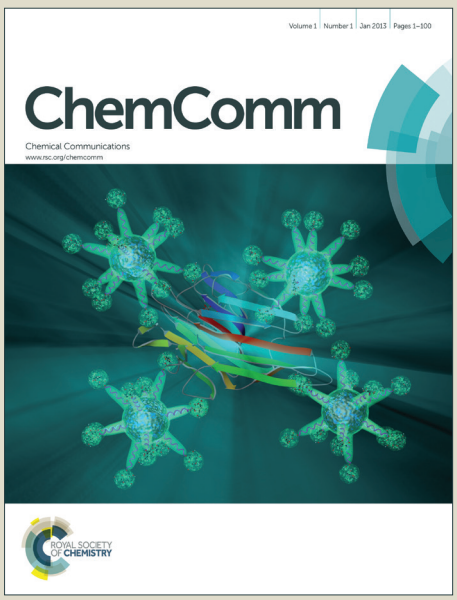

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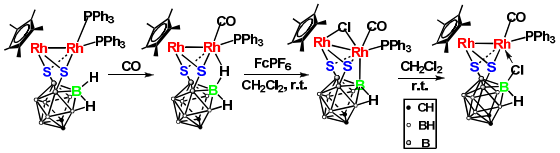

Metal-metal redox synergy is firstly introduced to B−H functionalization of inert dicarba-dodecaboranes under mild conditions in high yields.

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Metal−Metal Redox Synergy in Selective B−H Activation of *ortho*-Carborane-9,12-dithiolate

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New *o*-carborane-9,12-dithiolate dirhodium complexes are reported to selectively activate inert B−H bonds of *o*-carborane to form B−X bonds by using water, alcohols, alkylhalides (< 60 °C, yields > 80%). Characterization of key intermediates demonstrates oxidative addition and reductive elimination pathway via metal−metal cooperativity.

Carboranes have been used for decades in pharmaceuticals, materials and catalysis.[1−3] Functionalization of B−H bonds[4] is an important strategy for rapid generation of versatile carborane derivatives to enable these diverse applications. Metal-mediated hydroboration of carboranes have been reported as an important method for direct cage boron derivatization.[4,5] In view of the spectacular role of metals in functionalization of B−H bond, M−B bond formation is involved.[4−6] Note that B−H activation of small boranes[7] has been successful in which metal−boryl complexes serve as intermediates in C−H borylation. However, selective B−H activation of carboranes leading to B−H functionalization via a M−B bond is still challenging. To date, the scopes of substrates that are able to achieve B−H activation as well as further chemical transformations of intermediates containing a M−B bond represent major problems in the use of a single metal.[4−6]

Another strategy for B−H activation of carboranes is to use cooperative metal−metal (M−M) interactions inspired by Nature's highly efficient redox machinery on the basis of polynuclear active sites.[8] Thus, it is anticipated that metal−metal redox synergy may lower the energy barrier for the redox pathway of B−H activation and boron−heteroatom bond formation in comparison to single metal-mediated system.[4−6] However, examples for B−H activation at carboranes utilizing bimetallic redox synergy is not known. In the case of analogous C−H activation, the redox pathway at a single metal center has been well-established,[9] but the studies on the redox pathway at a two-metal model system is still rare[10]. For example, Ritter *et al* described bimetallic palladium complexes that can lower the energy barrier for C−H functionalization.[10a] Mankad *et al* reported C−H borylation utilizing bimetallic Cu−Fe/Zn−Fe cooperativity.[10b] Nevertheless, both examples involved metal−metal bond cleavage pathway in bimetallic redox cooperation owing to the orbital symmetry inhibition (Chart 1).[10c]

To evaluate the role of metal−metal redox synergy in B−H activation of inert carboranes, here, we report selective B−H activation and the further B−Cl and B−O bond formation in the *o*-carborane-9,12-dithiolate dirhodium complexes by using the common substrates such as CH_2Cl_2, $CHCl_3$, methanol and water. The characterization of new dirhodium complexes bearing Rh−H−B, Rh−B, Rh−H−Rh and Rh−Cl−Rh bonds has provided valuable mechanistic evidences on B−H activation through metal−metal redox synergy with unconventional variable metal–metal bond order in contrast to the metal–metal bond cleavage pathway (Chart 1).

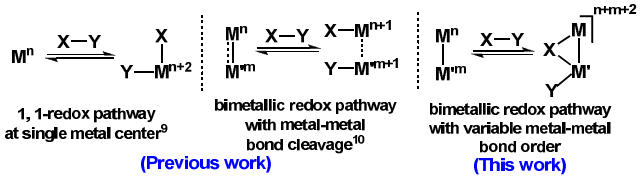


Chart 1. Illustration of redox pathways at single- and two-metal centers.

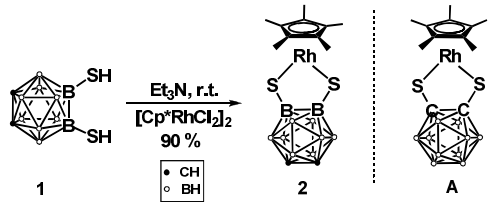
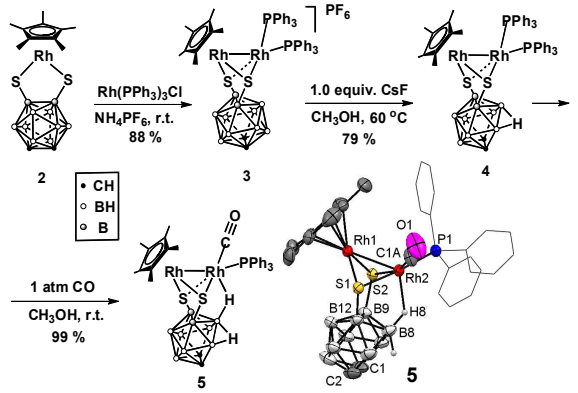


Fig. 1 (a) Synthesis of boron-substituted 16e complex **2** from *o*-carborane-9,12-dithiol (**1**) and schematic comparison of its structural analogous complex **A**.

o-Carborane-9,12-dithiol (**1**)[11] is suited for construction of 16e half sandwich complex **2**, analogous to previously well reported complex **A** [Cp*Rh{1,2-$S_2C_2(B_{10}H_{10})$}][12] (Cp* = η^5-C_5Me_5) (Fig. 1) prepared from *o*-carborane-1,2-dithiol. Complex **A** has been widely used as synthon[3d,5] that easily led to B−H activation at B(3)/B(6).[5] The analogous structure of **2** with S−B rather than S−C in **A**, however, shows different reaction chemistry at the Rh−S bonds that does not lead to B−H activation (SI-Scheme S1) likely due to the increased electron charge density at the sulfur atoms from the electron-donating carboranyl group.[13]



Scheme 1. Synthetic route to di-rhodium complexes bearing *o*-carborane-9,12-dithiolate ligand and molecular structure of **5**.

Thus dirhodium complexes were prepared, as shown in Scheme 1, to test the ability to induce B−H bond activation. After consideration of orbital symmetry inhibition[10c] in bimetallic redox pathways, $Rh(PPh_3)_3Cl$ was selected to react with **2** in the presence of NH_4PF_6 to give rise to dinuclear complex **3** (SI-Fig. S2). Deboronation of **3** under basic conditions afforded neutral complex **4** containing a *nido*-carborane unit (SI-Fig. S3). Both complexes **3** and **4** are stable in solid state but the Rh−PPh_3 bond is labile in solution, as reported in literature.[14] To evaluate the interaction between the B−H bond and metal centers, one bulky PPh_3 was replaced by CO, as a result, the carbonyl product 5 containing a Rh−H−B bond was generated in a quantitative yield (Scheme 1). The Rh2−H8 distance in **5** (2.075 Å) is much shorter than that (2.714 Å, SI-Fig. S3 and S4) in **4**, suggesting a strong interaction between the B−H bond and the Rh center in 5. In solution the ^{1}H {^{11}B} NMR spectrum shows the characteristic broad peak of Rh−H−B at −1.21 ppm consistent with the data in the known species bearing Rh−H−B bond.[4d] Correspondingly, the ^{11}B signal of Rh−H−B is significantly low-frequency shifted (> 5 ppm) in comparison to that in **4**. This gives an excellent example of the effect of steric factors on B−H activation.

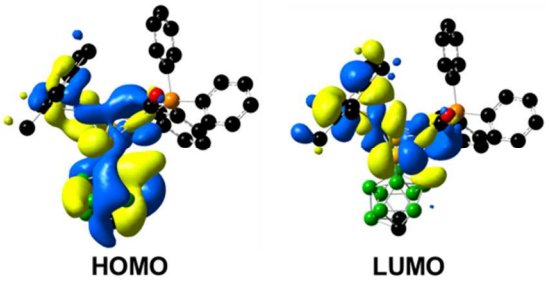
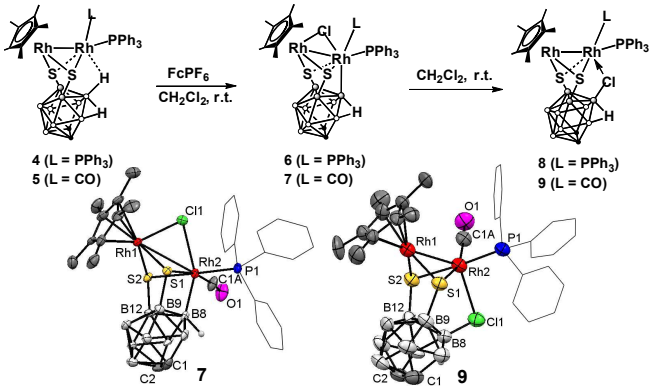


Fig. 2 Calculated molecular orbitals of 5 at B3PW91/6-31G(d, p)/LANL2DZ [Rh] level. The HOMO illustrated the Rh−Rh bonding orbitals whereas the LUMO exhibited the anti-bonding orbitals.

Structural determination of complex **5** provides a convincing model for calculating the bonding nature of Rh−H−B bond by DFT study. In Fig. 2, the HOMO (Highest Occupied Molecular Orbital) confirms the Rh−Rh binding in a non-symmetric fashion. The LUMO (Lowest Unoccupied Molecular Orbital) is mainly located at the metal cluster (73 %) and Cp* ring (22 %) but the orbital contribution of B(8)−H bond is not negligible (5 %). This predicts the potential nucleophilic attack of metal center toward the boron atom.



Scheme 2. B−H bond activation and B−Cl bond reductive elimination in the dirhodium complexes.

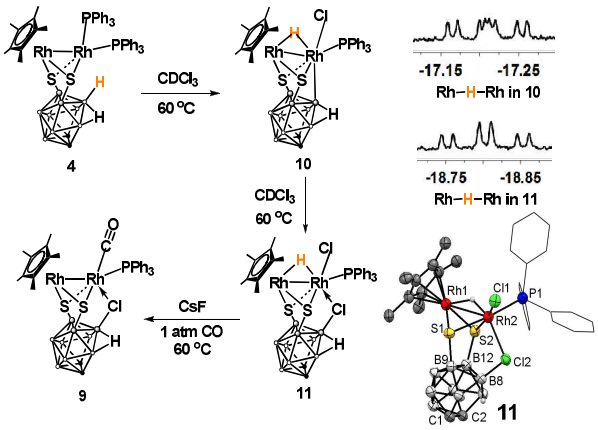
Treatment of complex **4** or **5** with 1.0 equiv. of $FcPF_6$ in CH_2Cl_2 at ambient temperature led to complex **6** or **7** which contains a Rh−B bond (Scheme 2, SI-Fig.S7). This demonstrates that the B−H bonds have been activated in both complexes in the presence of an oxidant and a chlorine source. The ^{11}B NMR resonances of the Rh−B units (−36.8 ppm in 6 and −39.7 ppm in 7) have been further low-frequency shifted (5 to 7 ppm) relative to those in 4 and 5. The solid-state structure of **7** exhibits a Rh−B bond (2.129 Å) and a Rh−Cl−Rh bond with extremely long Rh−Rh distance (3.157 Å, Scheme 2), in comparison to the Rh−Rh distances (2.584 to 3.232 Å) in known Rh−Cl−Rh species.[15]

The reductive elimination of **6** and **7** at ambient temperature yielded products **8** and **9** (Scheme 2), respectively, in high yields (> 80%) which contain a B−Cl bond and a normal Rh−Rh bond (2.739 Å for **8** and 2.688 Å for **9**, SI-Fig. S8 and S9), as confirmed by the X-ray structures. The ^{11}B NMR signals of B−Cl appear around 5.0 ppm in **8** and **9**, dramatically shifted to high frequency by over 40 ppm *vs.* those of the Rh−B bonds in **6** and **7**, further confirming B−Cl reductive elimination at the dirhodium centers. Note that other alkyl chlorides such as $CHCl_3$, $ClCH_2CH_2Cl$ and $PhCH_2Cl$ also react similarly. A radical pathway for chorine abstraction[16] may be involved as addition of Cl^- source (n-Bu_4NCl or $HCl_{(aq)}$) only led to decomposition of **4** or **5**.

Table 1. Listed Rh–Rh distances and WBI (Wiberg bond indices) values for **5**, **7**, **9** and **11**.

complex	5	7	9	11
Rh−Rh/Å (cry.)	2.7274(11)	3.1566(5)	2.6878(4)	2.6946(4)
Rh−Rh/Å (cal.)	2.773	3.228	2.716	2.722
WBI values	0.3054	0.0655	0.3517	0.2464

This is a standard sequence to demonstrate two-metal mediated B−H activation through adjusting Rh−Rh distance which is restored after B−Cl reductive elimination. To gain insights into electronic structure, a DFT calculation of complex **7** has been conducted which supports the low orbital symmetry in the Rh−Cl−Rh bonding scheme (SI-Fig. S24). The Wiberg bond indices (WBI) values were calculated for the Rh−Rh bond order and found to be 0.0655 in contrast to the much stronger Rh−Rh interactions in the precursor **5** (0.3054) and the product **9** (0.3517) (Table 1). Both structural determinations and theoretical calculations provide persuasive bond order support for reductive elimination from dimetal centers involving variable metal−metal bond order. This represents an unconventional metal−metal redox pathway in contrast to the metal−metal bond cleavage pathway[10a,b] in bimetallic redox chemistry (Chart 1).

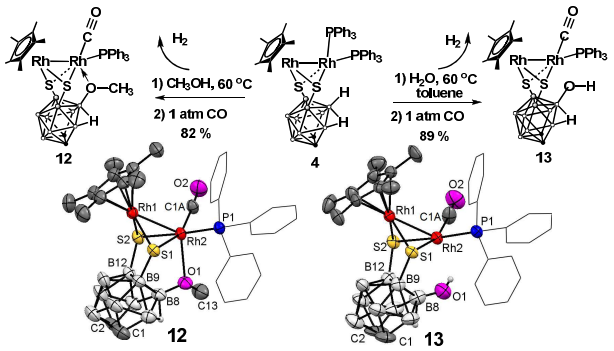


Scheme 3. Reactivity of complex **4** towards $CDCl_3$ at 60 ºC.

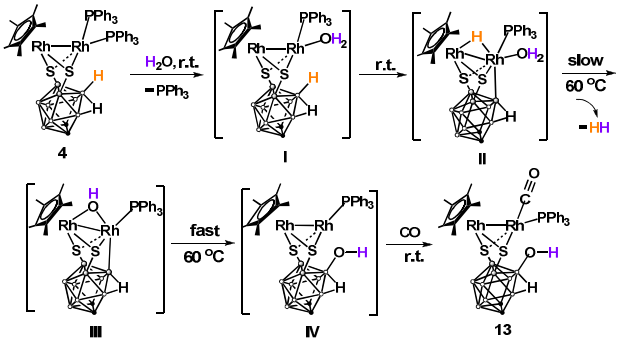
Above results demonstrate that an external oxidant (i.e. $FcPF_6$) facilitates B−H activation which occurs rapidly at room temperature. To better understand B−H activation at the very initial stages, complex 4 was heated in $CDCl_3$ at 60 ºC without addition of oxidant (Scheme 3) and this process was monitored by NMR and HRMS (SI-Fig. S13−16). The expected earlier intermediate bearing a Rh−H−B bond (δ = −3.69 ppm in ^{1}H {^{11}B} NMR) was detected in the first two hours (species **B** in SI-Fig. S11). Furthermore, complex **10** having both Rh−B and Rh−H−Rh bonds was observed which has a characteristic multiple hydride resonance ($^1J_{Rh1-H}$ = 20 Hz, $^1J_{Rh2-H}$ = 20 Hz, $^2J_{P-H}$ = 10 Hz) (Scheme 3). The Rh−B formation was confirmed by a distinctive low-frequency ^{11}B NMR signal at −40.3 ppm compared to the signals for B−H (−10.2 to −28.6 ppm) in **4**. The ESI-HRMS spectrum shows its molecular ion peak at 834.1007 for $[M+H^+]^+$ (SI-Fig. S16). The short life of **10** does not allow an additional structural characterization, but the spectral data is sufficient to state that B−H oxidative addition to di-rhodium centers has occurred. Complex **10** can cleanly convert to a new product **11** within 12 h in refluxing $CDCl_3$ (SI-Fig. S12 and S13). The hydride signal, a doublet of triplets at −18.80 ppm with $^1J_{Rh-H}$ = 20 Hz, $^2J_{P-H}$ = 10 Hz is typical of a bridging Rh−H−Rh bond (Scheme 3). The ^{11}B NMR signal of B−Cl (5.2 ppm) is shifted to high frequency by around 45 ppm *vs* Rh−B (−40.3 ppm) in 10. In solid state, the bridging hydride between Rh−Rh bond (Rh1−Rh2 2.695 Å, Rh−H 1.2921 and 1.7324 Å, Scheme 3, SI-Fig. S10) was identified by the electron density difference map.

The above results demonstrate the putative intermediate in di-rhodium mediated B−H activation to be species **10** containing a Rh−H−Rh bond, which is different from the conventional terminal hydride invoked in single-metal mediated[4c,7c] oxidative addition of a B−H bond. In general, the latter is more reactive. A Nature Bonding Orbital (NBO) analysis of **11** exhibits lower Rh−Rh bond order but shorter Rh−Rh bond length compared to **5** and **9** (Table 1). This indicates that the Rh−H−Rh bond possesses more anti-bonding character *vs* the conventional Rh−Rh bond, predicting the potential reactivity. Indeed, addition of carbon monoxide and CsF to **11** has led to product **9** (Scheme 3).

To further understand the role of metal−metal redox synergy in B−H activation, the reactivity of **4** was examined toward other substrates such as CH_3OH and water. The reaction of **4** and CH_3OH or water at 60 ºC followed by bubbling CO afforded **12** (82%) or **13** (89%), respectively (Scheme 4). Both structures feature a B−O bond (1.411 Å in **12**, and 1.424 Å in **13**, Scheme 4, SI-Fig. S11 and S12). The different electronic effects of methyl and hydrogen lead to different coordination fashion as indicated by Rh2···O1 distances in 12 (2.470 Å) and 13 (2.709 Å). The ^{11}B NMR signals of B−O have high-frequency shifted to 5.8 ppm in 12 and 4.4 ppm in **13** relative to −10.2 to −28.6 ppm for B−H in **4**. The formation of B−O bond in **13** demonstrates activation of both the inert B−H bond of carborane and the O−H bond of water under mild conditions has been achieved. This result should be attributed to the intriguing role of Rh−Rh redox synergy to lower energy barrier since direct B−O coupling between carborane and water has not been achieved by a single metal.



Scheme 4. Reactivity of complex **4** toward methanol and water.



Scheme 5. Proposed mechanism for the formation of B−O bond via activating both B−H bond of carborane and O−H bond of water.

To better understand this process, the reaction of **4** and H_2O was studied through monitoring by NMR and HRMS (for details, see SI-Section 4). As shown in Scheme 5, we propose that the reaction starts from ligand substitution of PPh_3 by H_2O (**I**) to initiate B−H oxidative addition (**II**) at ambient temperature, as occurred from **4** to **5** after release of bulky PPh_3. The formation of Rh−H−Rh hydride and Rh−B bond in **II** was detected by ^{1}H and ^{11}B NMR (SI-Fig. S17 and S19). The molecular ion peak of **I** and **II** was observed by HRMS to indicate the presence of the coordinate H_2O (SI-Fig. S18 and SI-Table S1). Then at an elevated temperature H_2 is released, followed by formation of **III**. Although this species was not observed by NMR probably owing to the short life, hydroxo-bridged dirhodium complexes derived from reactions of water and rhodium compounds have been described.[17] The generation of H_2 was confirmed by GC (SI-Fig. S21). Finally, B−O reductive elimination occurs to form **IV** which is stable and has been characterized by NMR and HRMS (SI-Fig. S19 and S20). Addition of CO leads to isolatable product **13**. Notably, water has been used as a clean oxygen or hydrogen supplier mediated by organometallic complexes,[18] however, dehydrogenetive B−O coupling of carborane using water with release of H_2 is not known. In addition, hydroxylation and chlorination of polyhedral boranes have been reported,[19] however, those

methods required demanding reaction conditions (H_2O_2/100 °C or N-chloimide/AcOH/150 °C) and tedious procedures. Here the new dinuclear metal-mediated B−H activation provides a promising approach to both B−Cl and B−O formation under mild conditions by using common substrates.

Conclusions

In conclusion, a new type of dirhodium complexes containing boron-substituted *nido-o*-carborane dithiolate has been developed. These complexes are able to selectively activate B−H bond at the B8 site of carborane and allow further functionalization to form B−Cl or B−O bond under mild conditions (<60 ºC) in isolated yields of over 80%. Characterization of both in-situ generated and isolated intermediate species containing Rh−H−B, Rh−B, Rh−H−Rh and Rh−Cl−Rh bonds strongly demonstrates metal−metal redox synergy in B−H functionalization in contrast to the reported single metal-induced B−H activation at B(3)/B(6) sites that usually led to B−C formation with yields of less than 50% owing to the presence of parallel pathways.[5] The mechanism of dehydrogenative B−O coupling between water and carborane also support metal−metal redox synergy. This work opens a door to efficient synthesis of carborane-functionalized derivatives at B(8) site.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Complete experimental procedures, spectral data for new compounds, calculation details and crystallographic data (CIF)]. See DOI: 10.1039/b000000x/

1 (a) N. S. Hosmane, *Boron Science*: New Technologies and Applications; CRC Press: Boca Raton, FL, 2011; (b) R. N. Grimes, *Carboranes* 2nd edition (Elsevier, 2011); (c) M. F. Hawthorne, *Angew. Chem. Int. Ed.* 1993, **32**, 950; (d) V. I. Bregadze, I. B. Sivaev, S. A. Glazun, *Anti-Cancer Agents Med. Chem.* 2006, **6**, 75; (e) J. Plešek, *Chem. Rev*. 1992, **92**, 269; (f) V. I. Bregadze, *Chem. Rev*. 1992, **92**, 209.

2 (a) B. P. Dash, R. Satapathy, E. R. Gaillard, J. A. Maguire, N. S. Hosmane, *J. Am. Chem. Soc.* 2010, **132**, 6578; (b) K. R. Wee, Y. J. Cho, J. K. Song, S. O. Kang, *Angew. Chem., Int. Ed.* 2013, **52**, 9682; (c) C. Shi, H. Sun, X. Tang, H. Lv, H. Yan, Q. Zhao, J. Wang, W. Huang, *Angew. Chem., Int. Ed*. 2013, **52**, 13434; (d) C. Masalles, J. Llop, F. Teixidor, *Adv. Mater.* 2002, **14**, 826; (e) K. Kokado, Y. Tokoro and Y. Chujo, *Macromolecules*, 2009, **42**, 2925; (f) M. Tominaga, Y. Morisaki, Y. Chujo, *Macromol. Rapid Commun.* 2013, **34**, 1357; (g) L. Weber J. Kahlert, R. Brockhine, L. Böhling, A. Brockhike, H. Stammler, B. Neumann, R. A. Harder, M. A. Fox, *Chem. Eur. J.* 2012, **18**, 8347.

3 (a) N. S. Hosmane, J. A. Maguire, In *Comprehensive Organometallic Chemistry III*; R. H. Crabtree and D. M. P. Mingos, Eds.; Elsevier: Oxford, 2007; Vol. 3, Chapter 5; (b) Z. Xie, *Acc. Chem. Res.* 2003, **36**, 1; (c) S. Liu, Y. F. Han, G. X. Jin, *Chem. Soc. Rev.* 2007, **36**, 1543; (d) Z. Qiu, S. Ren, Z. Xie, *Acc. Chem. Res*. 2011, **44**, 299.

4 (a) E. W. Corcoran, L. G. Sneddon, In *Advances in Boron and the Boranes*; J. F. Liebman, A. Greenberg, R. E. Williams, Eds.; VCH: New York, 1988, p 71; (b) D. Olid, R. Núñez, C. Viñas, F. Teixidor, *Chem. Soc. Rev.* 2013, **42**, 3318; (c) J. D. Hewes, C. W. Kreimendahl, T. B. Marder, M. F. Hawthorne, *J. Am. Chem. Soc.* 1984, **106**, 5757; (d) E. Molinos, G. Kociok-Kohn, A. S. Weller, *Chem. Comm.* 2005, 3609.

5 (a) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Angew. Chem., Int. Ed.* 1999, **38**, 3689; (b) R. Zhang, L. Zhu, G. Liu, H. Dai, Z. Lu, J. Zhao, H. Yan, *J. Am. Chem. Soc.* 2012, **134**, 10341; (c) Z. J. Wang, H. D. Ye, Y. G. Li, Y. Z. Li, H. Yan, *J. Am. Chem. Soc.* 2013, **135**, 11289; (d) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Chem. Eur. J.* 2002, **8**, 388.

6 (a) M. Liu, L. Dang, Z. Y. Lin, Z. W. Xie, *J. Am. Chem. Soc.* 2008, **130**, 16103; (b) Z. J. Yao, W. B. Yu, Y. J. Lin, S. L. Huang, Z. H. Li, G. X. Jin, *J. Am. Chem. Soc.* 2014, **136**, 2825; (c) A. M. Spokoyny, M. G. Reuter, C. L. Stern, M. A. Ratner, T. Seideman, C. A. Mirkin, *J. Am. Chem. Soc.* 2009, **131**, 9482.

7 (a) H. Y. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, *Science* 2000, **287**, 1992; (b) J. Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, M. R. Smith, *Science* 2002, **295**, 305; (c) S. Shimada, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *Angew. Chem. Int. Ed.* 2001, **40**, 2168; (d) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.*2010, **110**, 890.

8 (a) B. M. Hoffman, D. R. Dean, L. C. Seefeldt, *Acc. Chem. Res.* 2009, **42**. 609; (b) M. J. Corr, J. A. Murphy, *Chem. Soc. Rev.* 2011, **40**, 2279.

9 For reviews, see: (a) *Chem. Rev.* 2010, **110**, 575-1211, Issue name: selective functionalization of C−H bonds.

10 (a) D. C. Powers, T. Ritter, *Acc. Chem. Res.* 2012, **45**, 840; (b) T. J. Mazzacano, N. P. Mankad, *J. Am. Chem. Soc.* 2013, **135**, 17258; (c) G. Trinquler, R. Hoffmann, *Organometallics* 1984, **3**, 370; (d) T. G. Gray, A. S. Veige, D. G. Nocera, *J. Am. Chem. Soc.* 2004, **126**, 9760; (e) M. R. Radlauer, M. W. Day, T. Agapie, *J. Am. Chem. Soc.* 2012, **134**, 1478; (f) S. A. Reed, M. C. White, *J. Am. Chem. Soc.* 2008, **130**, 3316.

11 J. Plešek, Z. Janoušek, S. Heřmánek, *Coll. Czech. Chem. Comm.* 1980, **45**, 1775.

12 M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* 1999, **587**, 252.

13 (a) A. M. Spokoyny, C. W. Machan, D. C. Clingerman, M. S. Rosen, M. J. Wiester, R. D. Kennedy, A. A. Sarjeant, C. L. Stern, C. A. Mirkin, *Nat. Chem*. 2011, **3**, 590; (b) X. L. Zhang, X. Tang, J. Yang, Y. Li, H. Yan, V. I. Bregadze, *Organometallics* 2013, **32**, 2014.

14 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals (4th Edition ed.)*, 2005, Chapter 4.

15 (a) G. H. Chen, J. Y. Gui, L. C. Li, J. Liao, *Angew. Chem., Int. Ed.* 2011, **50**, 7681; (b) Z. Freixa, P. C. Kamer, M. Lutz, A. L. Spek, P. W. N. M. Leeuwen, *Angew. Chem., Int. Ed.* 2005, **44**, 4385.

16 (a) H. R. Dias, R. G. Browning, S. A. Polach, H. V. Diyabalanage, C. J. Lovely, *J. Am. Chem. Soc.* 2003, **125**, 9270; (b) Z. Csok, O. Vechorkin, S. B. Harkins, R. Scopelliti, X. Hu, *J. Am. Chem. Soc.* 2008, **130**, 8156; (c) J. Breitenfeld, J. Ruiz, M.D. Wodrich, X. L. Hu, *J. Am. Chem. Soc.* 2013, **135**, 12004.

17 (a) F. Chritensson, J. Springborg, *Inorg. Chem.* 1985, **24**, 2129; (b) A. Drljaca, A. Zahl, R. V. Eldik, *Inorg. Chem.* 1998, **37**, 3948.

18 (a) E. Balaraman, E. Khaskin, G. Leitus, D. Milstein, *Nat. Chem*. 2013, **5**, 123; (b) X. F. Fu, S. Li, B. B. Wayland, *J. Am. Chem. Soc.* 2006, **128**, 8947; (c) C. T. To, K. S. Choi, K. S. Chan, *J. Am. Chem. Soc.* 2012, **134**, 11388.

19 (a) T. Peymann, A. Herzog, C. B. Knobler, M. F. Hawthorne, *Angew. Chem., Int. Ed.* 1999, **38**, 1062; (b) O. V. Alekseenko, S. N. Dugin, E. L. Gurova, P. A. Storozhenko, RU2454422, 2012-06-27; (c) K. C. Kim, C. A. Reed, G. S. Long, A. Sen, *J. Am. Chem. Soc.* 2002, **124**, 7662.