Organic LETTERS

Letter

pubs.acs.org/OrgLett

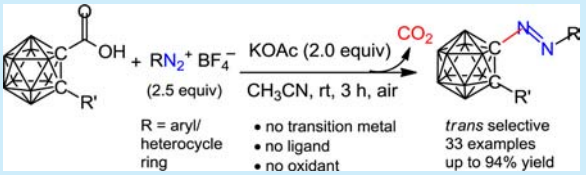
Base-Promoted Decarboxylative Azo-Coupling: Construction of Unsymmetrical Azocarboranes

Huan-huan Li,[†] Fan Bai,[†] Hong Yan,*[,†] and Chang-sheng Lu*[,†]

[†]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023 (P. R. China)

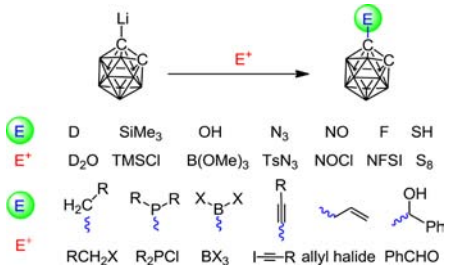
Supporting Information

ABSTRACT: Base-promoted decarboxylative azo couplings of carboranyl carboxylic acids with diazo salts have been developed to provide *trans*-azocarboranes in high yields (up to 94%). This approach is simple, efficient, and compatible with various functional groups. Mechanistically, the coupling has been proven to proceed in a nonradical pathway, which is distinct from those classical decarboxylative couplings.



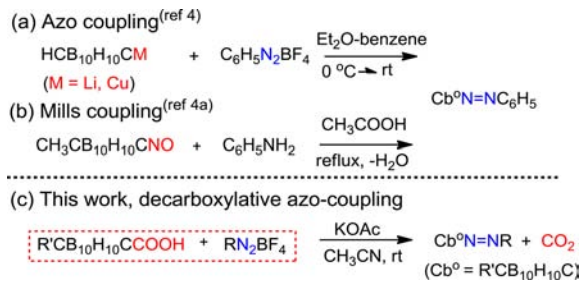
New methodologies for efficient C-functionalization of carboranes are still important area of research, although some approaches have been achieved principally via $B_{10}H_{12}L_2$[1] derivatives (L = CH_3CN, Et_2S), carboryne,[2] and lithiocarborane[3] (*o*-carboranyl carbanion equivalent). Among those, lithiocarborane showed high nucleophilic reactivity toward various electrophiles to yield C-substituted derivatives as depicted in Scheme 1.

Scheme 1. Reactions between Lithiocarborane and Electrophiles (E^+) Yield C-Substituted Carboranes



However, only a few examples had been reported to construct azocarboranes.[4] For instance, azo coupling of $HCB_{10}H_{10}CM$ (M = Li, Cu) with diazo salt (Scheme 2a) and Mills reaction of nitrosocarborane[3i] with aniline (Scheme 2b) allowed the direct synthesis of some substituted azocarboranes.[4] These couplings, however, were limited by narrow substrate scopes and unsatisfactory yields (<67%) due to the acidic media, redox-active nitroso functionality, or low reactivity of diazo salt in ether[5] and were, therefore, unsuitable to further elaboration. It was known that azo species performed key roles in ionic liquid−crystal materials,[6] therapeutic agents,[7] and direct functionalization.[8] To address the limitations of existing methods, we then turned our attention to decarboxylative coupling as a novel strategy for the synthesis of such compounds.

Scheme 2. Different Synthetic Routes to Azocarboranes



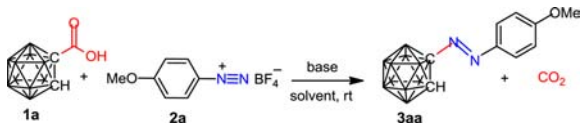
Decarboxylative couplings[9] are powerful strategies for a variety of transformations based on photoredox or metal catalysis, e.g., arylation,[10] olefination,[11] halogenation,[12] and azidation.[13] To the best of our knowledge, the carboxyl group served as a directing group which site-selectively functionalized cage B−H bonds via cyclometalation,[14] but it has never been used to synthesize azocarboranes through decarboxylation process (Scheme 2c). In this context, we chose 1-COOH-2-R′-*o*-$C_2B_{10}H_{10}$ as a coupling partner in place of sensitive $HCB_{10}H_{10}CM$ (M = Li, Cu) reagents because of their ready availability, air and moisture stability, easy operability, and importantly, their good tolerance to various functional groups. As a result, we developed the efficient synthesis of exclusive *trans*-azocarboranes in high yields by decarboxylative azo coupling. This reaction could proceed at ambient temperature in open air and circumvent the use of catalyst and oxidant.

Initially, the reaction of 1-COOH-*o*-$C_2B_{10}H_{11}$ (**1a**) with *p*-methoxybenzenediazonium fluoborate (**2a**) was conducted in the presence of Ag_2CO_3 alone (0.5 equiv) as a base in CH_3CN at room temperature for 3 h. The yellow product **3aa** (Table 1, entry 1) was obtained in 70% yield (by ^1H NMR) as the *trans*-isomer (Figure 1), which is thermodynamically stable.[4d,15] Byproducts *o*-carborane (18%) and anisole arising from the decarboxylation and dediazoniation[16] of both substrates were

Received: January 3, 2017
Published: February 1, 2017

DOI: 10.1021/acs.orglett.7b00013
Org. Lett. 2017, 19, 862−865

Table 1. Optimization of Reaction Conditions[a]



entry	base (equiv)	solvent	yield[b] (%)
1	Ag_2CO_3 (0.5)	CH_3CN	70
2		CH_3CN	nr
3[c]	Ag_2CO_3 (0.5)	CH_3CN	nr
4	Ag_2CO_3 (0.5)	acetone	56
5	Ag_2CO_3 (0.5)	toluene	nr
6	Ag_2CO_3 (0.5)	THF	nr
7	Ag_2O (0.5)	CH_3CN	53
8	AgOAc (1)	CH_3CN	78
9	Na_2CO_3 (1)	CH_3CN	74
10	K_2CO_3 (1)	CH_3CN	84
11	K_3PO_4 (1)	CH_3CN	76
12	Cs_2CO_3 (1)	CH_3CN	82
13	$Cu(OAc)_2$ (1)	CH_3CN	62
14	LiOAc (2)	CH_3CN	70
15	NaOAc (2)	CH_3CN	88
16	CsOAc (2)	CH_3CN	90
17	CsOPiv (2)	CH_3CN	86
18	KOAc (2)	CH_3CN	96 (94, air[d])
19	KF (2)	CH_3CN	72
20	DBU/Et_3N (1)	CH_3CN	nr

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), base, solvent (1.5 mL) for 3 h under Ar at room temperature. nr = no reaction. [b]Yields determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard. [c]Using *o*-$C_2B_{10}H_{12}$ instead of 1-COOH-*o*-$C_2B_{10}H_{11}$. [d]Reaction was performed under air.

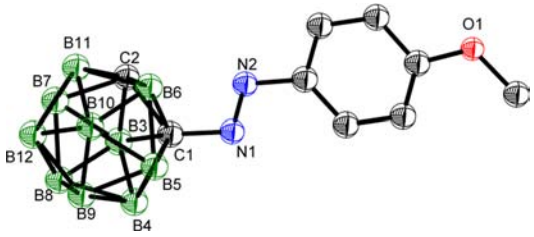
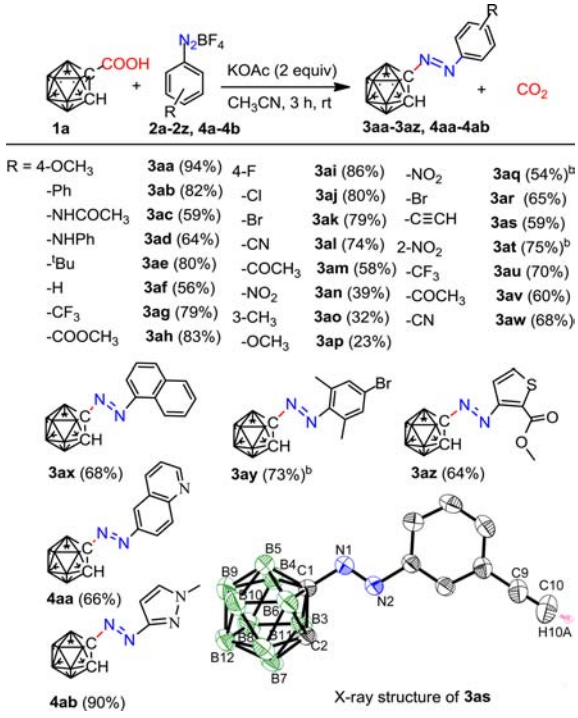


Figure 1. X-ray crystal structure of **3aa** (drawn with 50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

detected at the same time. Notably, product **3aa** was not formed without Ag_2CO_3 (Table 1, entry 2), indicating the crucial role of base. No such coupling took place between *o*-$C_2B_{10}H_{12}$ and **2a** in the presence of Ag_2CO_3 (Table 1, entry 3). This clearly suggested that the COOH group directly participated the process (entry 1 vs 3). The reaction efficiency was found to be dramatically affected by solvents (entries1 and 4−6 and Table S3). The polar solvent CH_3CN was the best (entry 1), perhaps owing to the increased solubility and electrophilicity of diazo salt.[17] To minimize side reactions, various inorganic bases were examined in detail (Table 1, entries 7−19). It appeared that KOAc was the best as the coupling reaction proceeded in almost quantitative conversion, delivering **3aa** in a high yield of 96% (entry 18). It was gratifying to find that the reaction could be carried out in open air to give a similar yield (94%). In addition, organic bases such as Et_3N and DBU, however, did not initiate the azo coupling (Table 1, entry 20). Therefore, the combination of 2 equiv of KOAc in CH_3CN under air at room temperature for 3 h served as the optimized conditions. In particular, neither transition-metal catalyst nor oxidant was required for this coupling reaction.

With the optimized conditions in hand, the scope of diazo salts was first examined (Scheme 3). Various diazo salts were coupled

Scheme 3. Structural Variation of Diazo Salts[a]



[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), KOAc (2.0 equiv), CH_3CN (1.5 mL) for 3 h under air at room temperature; the yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard. [b]1-COOH-2-Ph-*o*-carborane was used instead of 1-COOH-2-Me-*o*-carborane.

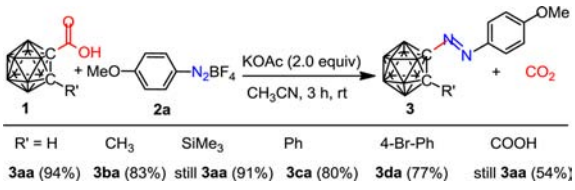
successfully with **1a** by our method, affording the corresponding *trans*-azocarboranes in good yields (>50%) except **3an−ap**. The reaction was sensitive to the electronic nature of the substituents on the aromatic ring. As for electron-rich or electron-neutral groups at the *para*-position, the higher yields of the azo products were generated, such as **3aa−ag**, whereas the strong electron-withdrawing group, for example, 4-NO_2, led to **3an** in a lower yield (39%). However, it was found that substrates containing electron-rich groups (**3ao**,**ap**) at the *meta*-position were much less reactive than those containing electron-withdrawing groups (**3aq−as**). Substrates containing sterically hindered substituents, such as a 2,6-dimethyl group (**3ay**), could be transferred with a good yield (73%).

Significantly, our method showed good functional group tolerance; for instance, amido, halo, cyano, trifluoromethyl, carbonyl, keto, as well as ester groups were all allowed. The unsaturated C≡CH triple bond (**3as**) remained unaffected by the process as well, which could enable subsequent functionalization (i.e., click reaction, Sonogashira coupling). In addition, diverse heterocyclic diazo salts including thiophene (**3az**), quinoline (**4aa**), and pyrazole (**4ab**) derivatives also underwent this coupling reaction, providing the corresponding azocarboranes in satisfactory yields (64%, 66%, and 90%, respectively). These results demonstrated the superiority of our method for the preparation of diverse azocarboranes.

DOI: 10.1021/acs.orglett.7b00013
Org. Lett. 2017, 19, 862−865

In addition, other monocarboranyl carboxylic acids reacted smoothly with **2a**, delivering the desired azo products in good to excellent yields (Scheme 4). The trimethylsilyl derivative reacted

Scheme 4. Structural Variation of Monocarboxylic Acids[a]



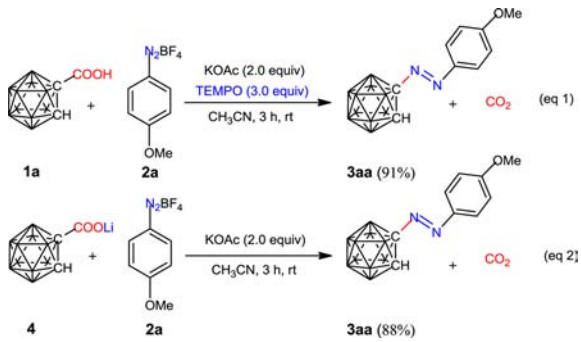
[a]Reaction conditions: **1** (0.1 mmol), **2a** (0.25 mmol), KOAc (2.0 equiv), CH_3CN (1.5 mL) for 3 h under air at room temperature; the yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

well under the same conditions with the removal of the trimethylsilyl unit (selective protection for C-monosubstituted carboranes), producing **3aa** in high yield (91%). When R′ was replaced by a COOH group, the mono azo coupling occurred selectively to afford **3aa** in a decreased yield (54%). In a sharp contrast, an aromatic acid such as benzoic acid failed to give any azobenzene under the same conditions (see the Supporting Information). This reactivity difference was due to the stronger electron-withdrawing ability of icosahedral *o*-carborane compared to the benzene moiety.[9−13,18] As a result, carboranyl carboxylic acids led to an relatively easier decarboxylation process under milder condition than those of benzoic acid.

In order to test the practicality of our method, gram-scale syntheses of **3aa** (1.28 g, 90% isolated yield), **3as** (0.71 g, 52% isolated yield), and **3az** (0.86 g, 55% isolated yield) were performed, which proved that such methodology could be efficiently scaled up. Note that, for safety a caution must be taken if a large amount of aryl diazo salts are used!

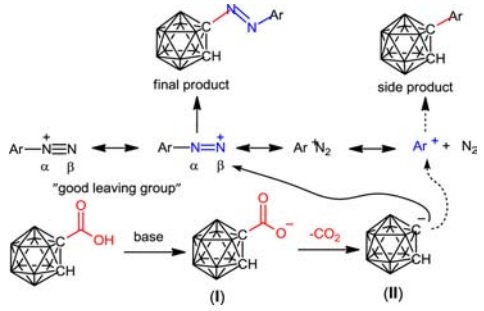
To clarify the mechanism, control experiments were performed (Scheme 5). When a radical scavenger TEMPO

Scheme 5. Control Experiments



(3.0 equiv) was added to the reaction mixture (eq 1), azo coupling reaction could not be inhibited and **3aa** was obtained in an excellent yield as well (91%). Therefore, the reaction practically proceeded via a nonradical pathway, in stark contrast to the radical-involved decarboxylative couplings.[9−13] As we expected, the reaction between 1-COOLi-*o*-$C_2B_{10}H_{11}$ (**4**) and **2a** also underwent azo coupling promoted by KOAc, providing **3aa** in 88% yield (eq 2). In addition, lithiocarborane was reported to react with benzenediazonium fluoroborate to afford azocarborane in the earliest work of Zakharkin et al.[4a] These results all supported our hypothesis outlined in Scheme 6. The carboxyl

Scheme 6. Proposed Mechanism for the Base-Promoted Decarboxylative Azo Coupling



group is first deprotonated by base and converted to a COO^- group, whose strong electron-donor properties favor the nucleophilicity[19] of *o*-carboranyl carbanion **II** (generated by decarboxylative activation of **I**). The intermediate **II** readily reacts with diazonium ion through a cation−anion combination reaction (see the Supporting Information for details). Thus, this type of pathway is analogous to those couplings of organometallics RM (M = MgX,[20a,b] ZnX,[20c] Li,[20d] etc.) with diazo salts. According to our results, azo coupling occurs quickly as **II** is reactive to electrophiles.[3,4] Decarboxylation (involving the cleavage of C_{cage}−COO bond) might be the key step.

Note that the azo couplings occur exclusively at the decarboxylation position (C vertex) rather than at the B site,[21] greatly different from that of $B_{10}H_{10}^{2-}$ dianions with diazo salts.[22] It is likely that this selectivity depends upon the regiospecificity of the reaction of *o*-carboranyl carbanion.

In conclusion, a series of *trans*-azocarboranes have been synthesized through a decarboxylative azo-coupling reaction. *o*-Carboranyl carbanion is promoted by weak base and shows high reactivity toward a broad range of diazo salts. Importantly, coupling proceeds under remarkably mild conditions (weak base, room temperature, in open air) and avoids the use of transition-metal catalyst and oxidant. It represents a new, simple, convenient, and effective alternative to previous procedures.

■ ASSOCIATED CONTENT

Supporting Information

TThe Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00013.

Experimental procedures, full characterization of products, NMR spectra, and X-ray crystallographic data (PDF)
X-ray data for **3aa**, **3ae**, **3ar**, and **3as** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: hyan1965@nju.edu.cn.
*E-mail: luchsh@nju.edu.cn.

ORCID

Hong Yan: 0000-0003-3993-0013

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21472086 and 21531004) and the National Basic Research Program of China (2013CB922101).

DOI: 10.1021/acs.orglett.7b00013
Org. Lett. 2017, 19, 862−865

REFERENCES

(1) (a) Li, Y. Q.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **2008**, *47*, 9193. (b) Toppino, A.; Genady, A. R.; El-Zaria, M. E.; Reeve, J.; Mostofian, F.; Kent, J.; Valliant, J. F. *Inorg. Chem.* **2013**, *52*, 8743. (c) El-Zaria, M. E.; Keskar, K.; Genady, A. R.; Ioppolo, J. A.; McNulty, J.; Valliant, J. F. *Angew. Chem.* **2014**, *126*, 5256. (d) Grimes, R. N. *Carboranes*, 2nd ed.; Academic Press: New York, 2011; Vol. *9*, pp 301.

(2) See reviews: (a) Qiu, Z. Z.; Xie, Z. W. *Dalton Trans.* **2014**, *43*, 4925. (b) Zhao, D.; Xie, Z. W. *Coord. Chem. Rev.* **2016**, *314*, 14. (c) Qiu, Z. Z.; Ren, S. K.; Xie, Z. W. *Acc. Chem. Res.* **2011**, *44*, 299.

(3) (a) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209. (b) Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Alexander, R. P.; Papetti, S.; Reid, J. A.; Trotz, S. I. *Inorg. Chem.* **1963**, *2*, 1097. (c) Boyd, L. A.; Clegg, W.; Copley, R. C. B.; Davidson, M. G.; Fox, M. A.; Hibbert, T. G.; Howard, J. A. K.; Mackinnon, A.; Peace, R. J.; Wade, K. *Dalton Trans.* **2004**, 2786. (d) Tsuji, M. *J. Org. Chem.* **2003**, *68*, 9589. (e) Hoel, E. L.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 6388. (f) Dozzo, P.; Kasar, R. A.; Kahl, S. B. *Inorg. Chem.* **2005**, *44*, 8053. (g) Kasar, R. A.; Knudsen, G. M.; Kahl, S. B. *Inorg. Chem.* **1999**, *38*, 2936. (h) Fox, M. A.; Cameron, A. M.; Low, P. J.; Paterson, M.; Batsanov, A. S.; Goeta, A. E.; Rankin, D.; Robertson, H. E.; Schirlin, J. T. *Dalton Trans.* **2006**, 3544. (i) Fox, M. A.; MacBride, J. A. H.; Peace, R. J.; Clegg, W.; Elsegood, M. R. J.; Wade, K. *Polyhedron* **2009**, *28*, 789. (j) Blanch, R. J.; Bush, L. C.; Jones, M. *Inorg. Chem.* **1994**, *33*, 198. (k) Kennedy, R. D. *Chem. Commun.* **2010**, *46*, 4782. (l) Kahlert, J.; Böhling, L.; Brockhinke, A.; Stammler, H.; Neumann, B.; Rendina, L.; Low, P. J.; Weber, L.; Fox, M. A. *Dalton Trans.* **2015**, *44*, 9766. (m) Hnyk, D.; Všetečka, V.; Drož, L. *J. Mol. Struct.* **2010**, *978*, 246. (n) Maurer, J. L.; Berchier, F.; Serino, A. J.; Knobler, C. B.; Hawthorne, M. F. *J. Org. Chem.* **1990**, *55*, 838. (o) Fey, N.; Haddow, M. F.; Mistry, R.; Orpen, A. G.; Reynolds, T. J.; Norman, N. C.; Pringle, P. G. *Organometallics* **2012**, *31*, 2907. (p) Gomez, F. A.; Hawthorne, M. F. *J. Org. Chem.* **1992**, *57*, 1384. (q) Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1167. (r) Ohta, K.; Ogawa, T.; Endo, Y. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 4728. (s) Galliamova, L. A.; Varaksin, M. V.; Chupakhin, O. N.; Slepukhin, P. A.; Charushin, V. N. *Organometallics* **2015**, *34*, 5285. (t) Axtell, J. C.; Kirlikovali, K. O.; Djurovich, P. I.; Jung, D.; Nguyen, V. T.; Munekiyo, B. A.; Royappa, T.; Rheingold, A. L.; Spokoyny, A. M. *J. Am. Chem. Soc.* **2016**, *138*, 15758.

(4) (a) Kalinin, V. N.; Zhigareva, G. G.; Zakharkin, L. I. *Synth. React. Inorg. Met.-Org. Chem.* **1972**, *2*, 105. (b) Kovredov, A. I.; Zakharkin, L. I. *Zh. Obshch. Khim.* **1986**, *56*, 2316. (c) Zakharkin, L. I.; Zhigarev, G. G. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1989**, *38*, 179. (d) Fox, M. A.; Peace, R. J.; Clegg, W.; Elsegood, M.; Wade, K. *Polyhedron* **2009**, *28*, 2359.

(5) (a) Juri, P. N.; Bartsch, R. A. *J. Org. Chem.* **1979**, *44*, 143. (b) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: London, 1989; p 920. (c) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: London, 1989; p 1227.

(6) (a) Ringstrand, B.; Monobe, H.; Kaszynski, P. *J. Mater. Chem.* **2009**, *19*, 4805. (b) Ringstrand, B.; Kaszynski, P.; Franken, A. *Inorg. Chem.* **2009**, *48*, 7313. (c) Ringstrand, B.; Kaszynski, P.; Young, V. G. *Inorg. Chem.* **2011**, *50*, 2654.

(7) (a) Hawthorne, M. F.; Wiersema, R. J.; Takasugi, M. *J. Med. Chem.* **1972**, *15*, 449. (b) Wong, H. S.; Tolpin, E. I.; Lipscomb, W. N. *J. Med. Chem.* **1974**, *17*, 785. (c) Leyden, R. N.; Hawthorne, M. F. *Inorg. Chem.* **1975**, *14*, 2444. (d) Ringstrand, B.; Kaszynski, P.; Young, V. G.; Janoušek, Z. *Inorg. Chem.* **2010**, *49*, 1166. (e) Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F. G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 1515.

(8) (a) Qian, C.; Lin, D.; Deng, Y. F.; Zhang, X. Q.; Jiang, H. F.; Miao, G.; Tang, X. H.; Zeng, W. *Org. Biomol. Chem.* **2014**, *12*, 5866. (b) Hubrich, J.; Himmler, T.; Rodefeld, L.; Ackermann, L. *ACS Catal.* **2015**, *5*, 4089. (c) Wangweerawong, A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2014**, *136*, 8520. (d) Xiong, F.; Qian, C.; Lin, D.; Zeng, W.; Lu, X. X. *Org. Lett.* **2013**, *15*, 5444. (e) Dong, J. W.; Jin, B.; Sun, P. P. *Org. Lett.* **2014**, *16*, 4540. (f) Li, J. X.; Zhou, H.; Zhang, J. L.; Yang, H. M.; Jiang, G. X. *Chem. Commun.* **2016**, *52*, 9589. (g) Zhang, D.; Cui, X. L.; Zhang, Q. Q.; Wu, Y. J. *J. Org. Chem.* **2015**, *80*, 1517. (h) Ryu, T.; Min, J.; Choi, W.; Jeon, W. H.; Lee, P. H. *Org. Lett.* **2014**, *16*, 2810. (i) Lian, Y. J.; Bergman, R. G.; Lavis, L. D.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 7122. (j) Hummel, J. R.; Ellman, J. A. *J. Am. Chem. Soc.* **2015**, *137*, 490. (k) Jeong, T.; Han, S. H.; Han, S.; Sharma, S.; Park, J.; Lee, J. S.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Org. Lett.* **2016**, *18*, 232.

(9) See reviews: (a) Liu, P.; Zhang, G. H.; Sun, P. P. *Org. Biomol. Chem.* **2016**, *14*, 10763. (b) Li, H. J.; Miao, T.; Wang, M.; Li, P. H.; Wang, L. *Synlett* **2016**, *27*, 1635. (c) Xuan, J.; Zhang, Z. G.; Xiao, W. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 15632. (d) Shen, C.; Zhang, P. F.; Sun, Q.; Bai, S. Q.; Hor, T. S. A.; Liu, X. G. *Chem. Soc. Rev.* **2015**, *44*, 291. (e) Zuo, Z. W.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. *Science* **2014**, *345*, 437. (f) Rodriguez, N.; Goossen, L. *Chem. Soc. Rev.* **2011**, *40*, 5030.

(10) (a) Goossen, L. J.; Rodríguez, N.; Melzer, B.; Linder, C.; Deng, G. J.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824. (b) Goossen, L. J.; Rodríguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248. (c) Shang, R.; Wang, Y.; Zhang, S.; Yang, Z. W.; Liu, L. *J. Am. Chem. Soc.* **2010**, *132*, 14391. (e) Hu, P.; Shang, Y. P.; Su, W. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 5945.

(11) (a) Tanaka, D.; Romeril, S. P.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 10323. (b) Hu, P.; Kan, J.; Su, W. P.; Hong, M. C. *Org. Lett.* **2009**, *11*, 2341. (c) Fu, Z. J.; Huang, S. J.; Su, W. P.; Hong, M. C. *Org. Lett.* **2010**, *12*, 4992. (d) Zhang, S. L.; Fu, Y.; Shang, R.; Guo, Q. X.; Liu, L. *J. Am. Chem. Soc.* **2010**, *132*, 638. (e) Jia, W.; Jiao, N. *Org. Lett.* **2010**, *12*, 2000. (f) Liu, X. S.; Wang, Z. T.; Cheng, X. M.; Li, C. Z. *J. Am. Chem. Soc.* **2012**, *134*, 14330. (g) Cui, L.; Chen, H.; Liu, C.; Li, C. Z. *Org. Lett.* **2016**, *18*, 2188.

(12) (a) Yin, F.; Wang, Z. T.; Li, Z. D.; Li, C. Z. *J. Am. Chem. Soc.* **2012**, *134*, 10401. (b) Wang, Z. T.; Zhu, L.; Yin, F.; Su, Z. Q.; Li, Z. D.; Li, C. Z. *J. Am. Chem. Soc.* **2012**, *134*, 4258. (c) Ventre, S.; Petronijevic, F. R.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2015**, *137*, 5654.

(13) (a) Zhu, Y. C.; Li, X. Y.; Wang, X. Y.; Huang, X. Q.; Shen, T.; Zhang, Y. Q.; Sun, X.; Zou, M. C.; Song, S.; Jiao, N. *Org. Lett.* **2015**, *17*, 4702. (b) Liu, C.; Wang, X. Q.; Li, Z. D.; Cui, L.; Li, C. Z. *J. Am. Chem. Soc.* **2015**, *137*, 9820.

(14) (a) Quan, Y. J.; Tang, C.; Xie, Z. W. *Chem. Sci.* **2016**, *7*, 5838. (b) Lyu, H. R.; Quan, Y. J.; Xie, Z. W. *Angew. Chem., Int. Ed.* **2016**, *55*, 11840. (c) Lyu, H. R.; Quan, Y. J.; Xie, Z. W. *J. Am. Chem. Soc.* **2016**, *138*, 12727.

(15) Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335.

(16) (a) Laali, K. K.; Okazaki, T.; Bunge, S. D. *J. Org. Chem.* **2007**, *72*, 6758. (b) Haghbeen, K.; Tan, E. W. *J. Org. Chem.* **1998**, *63*, 4503. (c) Kornblum, N.; Kelley, A. E.; Cooper, G. D. *J. Am. Chem. Soc.* **1952**, *74*, 3074.

(17) Mayr, H.; Hartnagel, M.; Grimm, K. *Liebigs Ann./Recl.* **1997**, *1997*, 55.

(18) (a) Spokoyny, A. M.; Machan, C. W.; Clingerman, D. J.; Rosen, M. S.; Wiester, M. J.; Kennedy, R. D.; Stern, C. L.; Sarjeant, A. A.; Mirkin, C. A. *Nat. Chem.* **2011**, *3*, 590. (b) Weller, A. *Nat. Chem.* **2011**, *3*, 577. (c) Spokoyny, A. M.; Lewis, C. D.; Teverovskiy, G.; Buchwald, S. L. *Organometallics* **2012**, *31*, 8478. (d) Teixidor, F.; Barberà, G.; Vaca, A.; Kivekäs, R.; Sillanpää, R.; Oliva, J.; Viñas, C. *J. Am. Chem. Soc.* **2005**, *127*, 10158.

(19) (a) Vauquelin, G.; Strosberg, A. D. *Clin. Chem.* **1976**, *22*, 1955. (b) Curtin, D. Y.; Tveten, J. L. *J. Org. Chem.* **1961**, *26*, 1764.

(20) (a) Garst, M. E.; Lukton, D. *Synth. Commun.* **1980**, *10*, 155. (b) Cohen, T.; Lewarchik, R.; Tarino, J. Z. *J. Am. Chem. Soc.* **1974**, *96*, 7753. (c) Curtin, D. Y.; Ursprung, J. A. *J. Org. Chem.* **1956**, *21*, 1221. (d) Hansen, M. J.; Lerch, M. M.; Szymanski, W.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2016**, *55*, 13514.

(21) Zollinger, H. *Diazo Chemistry I: Aromatic and Heteroaromatic Compounds* **1994**, 346.

(22) (a) Hawthorne, M. F.; Olsen, F. P. *J. Am. Chem. Soc.* **1964**, *86*, 4219. (b) Hawthorne, M. F.; Olsen, F. P. *J. Am. Chem. Soc.* **1965**, *87*, 2366.

DOI: 10.1021/acs.orglett.7b00013
Org. Lett. 2017, 19, 862−865