Organic LETTERS

Letter

pubs.acs.org/OrgLett

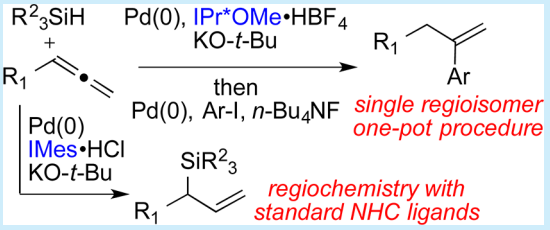
Regioselective Allene Hydroarylation via One-Pot Allene Hydrosilylation/Pd-Catalyzed Cross-Coupling

Zachary D. Miller and John Montgomery*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109-1055, United States

Supporting Information

ABSTRACT: Advances in hydroarylation have been achieved by the development of a one-pot regioselective allene hydrosilylation/Pd(0)-catalyzed cross-coupling protocol. The regioselectivity is primarily governed by *N*-heterocyclic carbene (NHC) ligand identity in the hydrosilylation step and is preserved in the subsequent cross-coupling reaction. This methodology affords streamlined access to functionalized 1,1-disubstituted alkenes with excellent regiocontrol.

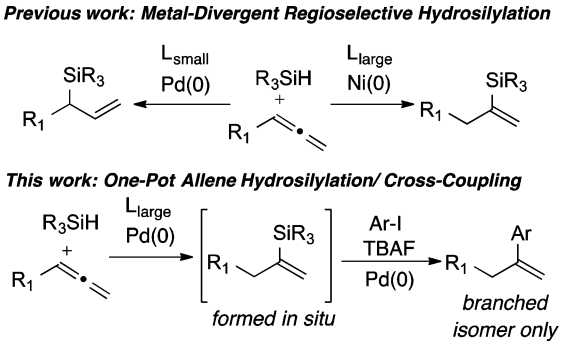


Alkenylsilanes are versatile nucleophiles in metal-catalyzed cross-coupling reactions. Numerous carbon−carbon bond-forming reactions with alkenylsilanes have been well developed,[1] including the powerful cross-coupling methodology extensively developed by Hiyama and Denmark.[2−4] Currently, the most direct routes to alkenylsilanes are via metal-catalyzed hydrosilylations of alkynes.[5] However, subtle alterations in the π-component, silane coupling partner, and metal catalyst often have substantial effects on the reaction outcome, leading to challenges in regiocontrol.[1a] Significant progress has been made in accessing alkenylsilane structures through the development of alternative methods, including reactions that introduce the silane moiety through carbon framework rearrangements,[6a,b] Heck[6c] and silyl-Heck reactions,[6d,e] or by nucleophilic additions to electrophilic halosilanes.[6f] However, the regio- and stereoselective addition of silanes to simple π-components remains an especially attractive point of entry to this structure class.

As a part of our laboratory's interests in developing regioselective catalytic processes,[7] we set out to explore catalytic allene hydrosilylation with the goal to discover conditions that would provide highly selective access to either allylsilanes or alkenylsilanes depending on the metal−ligand combination employed. Our previous work in regioselective allene hydrosilylations demonstrated that the selection of metal is an effective tool for gaining access to either allylsilanes with palladium NHC complexes or alkenylsilanes with nickel NHC complexes (Scheme 1).[7e] While the nickel-based procedure provided useful access to alkenylsilanes, the scope was somewhat limited, and access to the classes of alkenylsilanes that are most useful in cross-coupling methodology was not obtained. This inspired us to search for conditions with palladium catalysis where the inherent preference for allylsilane production could be reversed to allow alkenylsilane synthesis by simple alteration of the *N*-heterocyclic carbene ligand employed.

As additional motivation, identification of a palladium-catalyzed entry to alkenyl silanes from allenes would potentially allow a one-pot procedure to be developed involving regioselective allene hydrosilylation followed directly by a Pd-catalyzed cross-coupling event to provide a net hydroarylation process. Although significant progress has been achieved in one-pot alkyne hydroarylations with zinc[8a−c] and tin,[8d] one-pot hydroarylations involving hydrosilylation/cross-coupling sequences typically provide 1,2-disubstituted alkenes and often require purification of the alkenyl silane.[9] To address the above challenges, we report herein a general one-pot hydroarylation procedure that utilizes a catalyst-controlled regioselective allene hydrosilylation reaction in tandem with Pd-catalyzed cross-couplings to provide functionalized 1,1-disubstituted alkenes with exceptional regiocontrol (Scheme 1).

Scheme 1. Goals of the Current Study

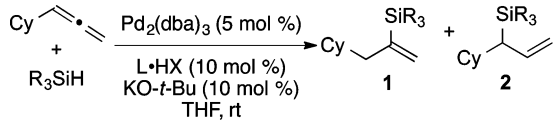


Our efforts to identify the conditions that favor alkenylsilanes in palladium-catalyzed allene hydrosilylation began with an evaluation of the effects of structural modification of NHC ligands on reaction outcome. To facilitate rapid screening, we utilized a protocol where the active catalyst is formed by the deprotonation of the NHC hydrochloride salt with an equivalent of KO-*t*-Bu base and Pd_2dba_3 precatalyst (Table 1). Our preliminary experiments resulted in the observation that methyl substitution of the backbone of *N*-mesityl ligands resulted in a

Received: September 18, 2014
Published: October 2, 2014

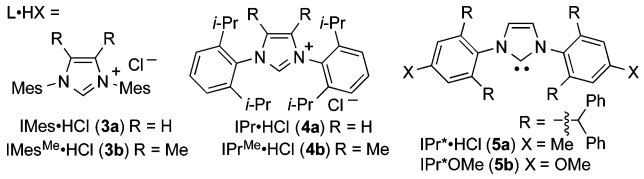
dx.doi.org/10.1021/ol502766q | *Org. Lett.* 2014, 16, 5486−5489

Table 1. Ligand Effects in Allene Hydrosilylation



entry	silane	L·HX	major product (% yield)	regioselectivity (1:2)
1	Et_3SiH	**3a**	**2a** (80)	<2:>98
2	Et_3SiH	**3b**	**2a** (85)	2:98
3	Et_3SiH	**4a**	**2a** (75)	12:88
4	Et_3SiH	**4b**	**1a** (83)	>98:2
5	Et_3SiH	**5a**	**1a** (50)	>98:2
6	Et_3SiH	**5b**[a]	**1a** (90)	>98:2
7	$BnMe_2SiH$	**4a**	**2b** (77)	3:97
8	$BnMe_2SiH$	**4b**	**1b** (73)	75:25[b]
9	$BnMe_2SiH$	**5a**	**1b** (62)	81:19
10	$BnMe_2SiH$	**5b**[a]	**1b** (79)	95:5

[a]Reaction conducted in the absence of KO-*t*-Bu. [b]Reaction conducted with 2.5 mol % Pd_2dba_3 and 5.0 mol % ligand.



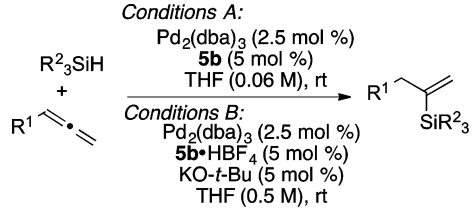
slight erosion of regioselectivity, with allylsilanes strongly preferred in analogy with our prior findings.[7e] For example, the hydrosilylation of cyclohexylallene with triethylsilane using IMes (**3a**) as a ligand resulted in excellent regioselectivities (>98:2) favoring allylsilane **2**, while use of $IMes^{Me}$ (**3b**) as a ligand proceeded with slightly decreased regioselectivity (98:2) in an excellent chemical yield of 85% (Table 1, entries 1 and 2).

The effects of NHC ligand variation were further explored with bulkier ligands (Table 1, entries 3−5). The reaction with the comparatively large IPr (**4a**) as the ligand still resulted in the allylsilane **2** as the major product with triethylsilane in 88:12 regioselectivity (Table 1, entry 3). However, use of IPr^{Me} (**4b**) as the ligand, modified from its IPr variant by simple dimethyl substitution of the backbone, afforded alkenylsilane **1** with triethylsilane in >98:2 regioselectivity in 83% yield. While the steric differences of IPr and IPr^{Me} have been previously recognized including a description of $\%V_{bur}$ for silver and gold complexes,[10a] this dramatic regiochemical reversal is nonetheless surprising.[10b] Additionally, variation of *N*-aryl rather than the backbone substituent also allows alkenyl silanes to be produced with exceptional regiocontrol. Specifically, the use of commercially available NHC carbene ligand IPr* (**5a**) or IPr*OMe (**5b**)[11] also provided a highly selective entry to alkenyl silanes, with product **1** being obtained again in >98:2 regioselectivity in both instances.

Given that an important objective of the current study is the utilization of organosilicon structures that perform well in cross-couplings, related hydrosilylations using $BnMe_2SiH$ were next examined (Table 1, entries 6−8). The comparison of IPr (**4a**), IPr^{Me} (**4b**), IPr* (**5a**), and IPr*OMe (**5b**) exhibited similar trends, with ligand **4a** providing allylsilane **2** with 97:3 regioselectivity, ligand **4b** providing a 75:25 mixture favoring alkenylsilane **1**, ligand **5a** favoring alkenylsilane **1** with 81:19 selectivity, and ligand **5b** favoring alkenylsilane **1** with optimum 95:5 regiocontrol. The **5a**:**5b** comparison illustrates that both the steric and electronic environment play an important role in regioselectivity. Given the superior regioselection of alkenylsilane production with IPr*OMe (**5b**) across the two different silane structures, this procedure was adopted as the standard procedure for alkenylsilane synthesis for the remainder of this study.

Variations in the silane coupling partner and allene substitution were then explored with the optimized procedure using ligand IPr*OMe (**5b**) as the free carbene (conditions A). Hydrosilylations occurred in 1−2 h at rt with palladium catalysis to afford a range of alkenylsilanes with a high degree of regiocontrol (Table 2). With the allene variations depicted,

Table 2. Silane and Allene Variation



entry	R^1	conditions	silane	product (% yield)	regioselectivity (1:2)
1	Cy	A	Me_2PhSiH	**1c** (90)	>98:2
2	Cy	A	$Me_2EtOSiH$	**1d** (81)	96:4
3	Ph	A	Me_2PhSiH	**6a** (83)	>98:2
4	Ph	A	$Me_2EtOSiH$	**6b** (88)	>98:2
5	Ph	A	$BnMe_2SiH$	**6c** (90)	>98:2
6	BnO	A	Me_2PhSiH	**7a** (95)[a]	>98:2
7	BnO	A	$Me_2EtOSiH$	**7b** (84)	>98:2
8	BnO	A	$BnMe_2SiH$	**7c** (85)	>98:2
9	*n*-Oct	A	Me_2PhSiH	**8a** (83)	98:2
10	*n*-Oct	A	$Me_2EtOSiH$	**8b** (87)	96:4
11	*n*-Oct	A	$BnMe_2SiH$	**8c** (91)	93:7
12	Cy	B	$BnMe_2SiH$	**1b** (94)	98:2
13	Cy	B	$Me_2EtOSiH$	**1d** (99)	98:2
14	Ph	B	$Me_2EtOSiH$	**6b** (94)	>98:2
15	Ph	B	$BnMe_2SiH$	**6c** (92)	>98:2

[a]Reaction was conducted on a 6.8 mmol scale.

Me_2PhSiH[12a] and $BnMe_2SiH$[12b] were explored due to their previous applications in cross-couplings, and $Me_2EtOSiH$ was also examined, as recent studies have demonstrated that this motif is effective in both fluoride-promoted and fluoride-free cross-couplings.[12c] The hydrosilylation of cyclohexylallene with Me_2PhSiH afforded product **1c** in 90% yield with Me_2PhSiH (Table 2, entry 1) while the reaction with $Me_2EtOSiH$ afforded alkenylsilane **1d** in 81% yield with high regioselectivity (96:4) (Table 2, entry 2). Aromatic allene substituents were well-tolerated with high regioselectivity (>98:<2) for each of the three silanes to afford **6a**−**6c** in excellent yields (Table 2, entries 3−5). Similarly, a benzyloxy-substituted allene was also well-tolerated with each of the silanes screened to yield alkenylsilanes **7a**−**7c** in excellent yields and regioselectivities (Table 2, entries 6−8). The ease of scale-up was examined for product **7a**, which was afforded in 95% yield in 6.8 mmol scale (Table 2, entry 6). Simple unhindered aliphatics were also well-tolerated with a slight erosion of regioselectivity to form products **8a**−**8c** with excellent yields and regioselectivities (Table 2, entries 9−11).

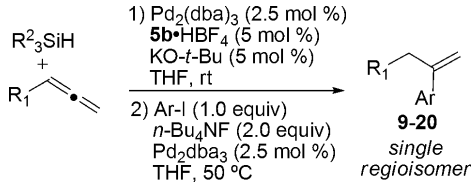
Improved reaction conditions were optimized to include standard benchtop assembly, without the use of air-free technology such as use of a glovebox (conditions B, Table 2). This protocol employs IPr*OMe·HBF_4 salt **5b**, KO-*t*-Bu base,

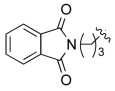
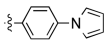
dx.doi.org/10.1021/ol502766q | *Org. Lett.* 2014, 16, 5486−5489

Pd_2dba_3 precatalyst, and more concentrated reaction conditions (0.5 M in THF). Reactions performed under these conditions were faster and higher yielding than with conditions A (Table 2). For example, four cases examined resulted in higher yields and improved regioselectivities compared with the analogous condition A experiments (Table 2, entries 12−15).

In parallel with our goal to develop a user-friendly hydroarylation protocol, we explored the use of optimum reaction conditions B in tandem with a cross-coupling reaction with electrophilic iodides (Table 3). In this procedure, the hydrosilylation reaction is monitored, and upon complete consumption of allene, tetra-*n*-butylammonium fluoride (TBAF), an iodide electrophile, and an additional 2.5 mol % Pd_2dba_3 precatalyst are added to the reaction mixture. The subsequent cross-coupling reaction occurs within 30 min, affording hydroarylation products **9**−**18** without detection of alkene isomers (Table 3). Although in very few cases there is slight formation of regioisomeric allylsilanes, these isomers do not afford cross-coupled minor isomers in the hydroarylation manifold likely due to competing protodesilylation.

Table 3. Regioselective Allene Hydroarylations



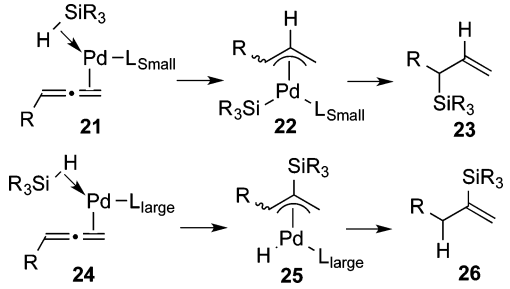
entry	R_1	silane	Ar-I	major product (% yield)
1	Cy	$Me_2EtOSiH$	Ph	**9** (95)
2	Cy	$BnMe_2SiH$	Ph	**9** (85)
3	Cy	$Me_2EtOSiH$	*p*-NO_2Ph	**10** (77)
4	Cy	$Me_2EtOSiH$	*p*-MeCOPh	**11** (90)
5	Cy	$Me_2EtOSiH$	*p*-MeOPh	**12** (74)
6	Cy	$Me_2EtOSiH$		**13** (81)
7	Cy	$Me_2EtOSiH$		**14** (77)
8	*n*-Oct	$Me_2EtOSiH$	*o*-tolyl	**15** (92)
9	Ph	$Me_2EtOSiH$	Ph	**16** (76)
10	Ph	$Me_2EtOSiH$		**17** (83)
11	BnO	$Me_2EtOSiH$	Ph	**18** (89)
12		$Me_2EtOSiH$		**19** (89)
13	*n*-Oct	$Me_2EtOSiH$	Ph	**20** (88)[a]

[a]Reaction was conducted on a 4.5 mmol scale without the second charge of $Pd_2(dba)_3$.

The scope of the one-pot hydroarylation reaction is general and provides access to a variety of 1,1-disubstituted alkenes. This method tolerates variation in silane structure, as $BnMe_2SiH$ and $Me_2EtOSiH$ were successfully coupled with PhI in high yields of 95% and 85% respectively (Table 3, entries 1 and 2). Aryl iodides with electron-withdrawing substituents (Table 3, entries 3 and 4) and electron-rich groups (Table 3, entry 5) were successfully coupled in excellent yields. In addition, a variety of heterocyclic-containing iodides functioned under the reaction conditions, as reactions with uracil-containing (Table 3, entry 6) and thienyl-containing (Table 3, entry 7) iodides were tolerated with excellent yields. More hindered substrates such as 2-iodotoluene provided the expected product **15** in excellent yield (Table 3, entry 8). Alterations in allene substitution had insignificant impact on the outcome of the reaction, as aromatic allenes were coupled with PhI (Table 3, entry 9, **16**) and oxacyclic moieties (Table 3, entry 10, **17**) in excellent yields of 76% and 83%. Additionally, a benzyloxy-substituted allene was successfully coupled with PhI in high yield (Table 3, entry 11, **18**). A phthalimido-containing allene was coupled with pyrrole-containing iodide to furnish hydroarylation product **19** in an excellent yield of 89% (Table 3, entry 12). While yields were typically optimum with an additional charge of palladium prior to the cross-coupling step, this was not required in a larger scale illustration using undeca-1,2-diene and phenyl iodide (Table 3, entry 13).

The mechanism and origin of regiochemistry reversal likely derives from changing from a hydrometalation to a silylmetalation pathway (Scheme 2). Our prior studies illustrated that the typical mode of addition in Pd-catalyzed hydrosilylations of allenes favors allylsilane production, consistent with delivery of the metal hydride to the allene central carbon. Typical NHC ligands such as IMes (**3a**) and IPr (**4a**) favor the production of allylsilanes by this route (**21** to **23**). In contrast, less common bulkier ligands such as IPr^{Me} (**4b**) or IPr*OMe (**5b**) more effectively introduce steric repulsion between the organosilane and ligand and reverse the pathway to favor alkenylsilane production through silyl addition to the central allene carbon (**24** to **26**). Significant insights in the mechanism and regiochemistry of related catalyzed additions to allenes come from the work of Morken and Suginome involving additions of diboranes or silylboranes.[13] A recent computational study of allene hydrosilylations proposed that cleavage of the Si−H bond and addition to the allene central carbon proceed in a single step.[14]

Scheme 2. Origin of Regioselectivity Governed by Ligand Size



In summary, careful selection of NHC ligand structure allows excellent regiocontrol in allene hydrosilylations with palladium catalysis, favoring either allylsilane or alkenylsilane products. While common NHC ligands favor allylsilane production, a variety of alkenylsilanes may be produced with the extremely bulky IPr*OMe ligand. This methodology utilizes standard benchtop assembly and achieves exceptional regiocontrol without the use of directing groups or electronic substrate biases. Highlights of this approach have been applied to the development of a one-pot hydroarylation reaction that combines the regioselective hydrosilylation strategy with a Pd(0)-catalyzed cross-coupling reaction of aryl and hetereocyclic iodides. This

dx.doi.org/10.1021/ol502766q | *Org. Lett.* 2014, 16, 5486−5489

hydroarylation method provides streamlined access to branched isomers in excellent yields without the requirement of isolation of alkenylsilane intermediates.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jmontg@umich.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Institutes of Health (GM57014). The laboratory of J. P. Wolfe (University of Michigan, Ann Arbor, MI) is thanked for the gift of aryl iodides used in preliminary optimization studies.

■ REFERENCES

(1) (a) Lim, D. S. W.; Anderson, E. A. *Synthesis* **2012**, *44*, 983−1010. (b) Blumenkopf, T. A.; Overman, L. E. *Chem. Rev.* **1986**, *86*, 857−873. (c) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375−1408. (d) Ojima, I.; Li, Z. Y.; Zhu, J. W. *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: Chichester, U.K., 1998; Vol. 2, pp 1687−1792.

(2) (a) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893−4901. (b) Chang, W.-T. T.; Smith, R. C.; Regens, C. S.; Bailey, A. D.; Werner, N. S.; Denmark, S. E. *Org. React.* **2011**, *75*, 213−745.

(3) (a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1989**, *54*, 268−270. (b) Tamao, K.; Kobayashi, K.; Ito, Y. *Tetrahedron Lett.* **1989**, *30*, 6051−6054. (c) Itami, K.; Nokami, T.; Ishimura, Y.; Mitsudo, K.; Kamei, T.; Yoshida, T. J.-I. *J. Am. Chem. Soc.* **2001**, *123*, 11577−11585. (d) Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565−568. (e) Hirabayashi, K.; Mori, A.; Kawashima, J.; Suguro, M.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 5342−5349. (f) Denmark, S. E.; Kobayashi, T. *J. Org. Chem.* **2003**, *68*, 5153−5159.

(4) For representative complex examples: (a) Denmark, S. E.; Fujimori, S. *J. Am. Chem. Soc.* **2005**, *127*, 8971−8973. (b) Denmark, S. E.; Liu, J. H.-C.; Muhuhu, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 14188−14189. (c) Trost, B. M.; Stivala, C. E.; Hull, K. L.; Huang, A.; Fandrick, D. R. *J. Am. Chem. Soc.* **2014**, *136*, 88−91.

(5) (a) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38−41. (b) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726−12727. (c) Ball, Z. T.; Trost, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 17644−17655. (d) Rooke, D. A.; Ferreira, E. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3225−3230. (e) Berthon-Gelloz, G.; Schumers, J.; De Bo, G.; Markó, I. E. *J. Org. Chem.* **2008**, *73*, 4190−4197. (f) Kawasaki, Y.; Ishikawa, Y.; Igawa, K.; Tomooka, K. *J. Am. Chem. Soc.* **2011**, *133*, 20712−20715. (h) Chaulagain, M. R.; Mahandru, G. M.; Montgomery, J. *Tetrahedron* **2006**, *62*, 7560−7566. (i) Ding, S.; Song, L.-J.; Chung, L. W.; Zhang, X.; Sun, J.; Wu, Y.-D. *J. Am. Chem. Soc.* **2013**, *135*, 13835−13842.

(6) (a) Grimm, J. B.; Otte, R. D.; Lee, D. *J. Organomet. Chem.* **2005**, *690*, 5508−5516. (b) Denmark, S. E.; Yang, S.-M. *Org. Lett.* **2001**, *3*, 1749−1752. (c) Minami, T.; Nishimoto, A.; Hanaoka, M. *Tetrahedron Lett.* **1995**, *36*, 9505−9508. (d) Martin, S. E.; Watson, D. A. *J. Am. Chem. Soc.* **2013**, *135*, 13330−13333. (e) McAtee, J. R.; Martin, S. E.; Ahneman, D. T.; Johnson, K. A.; Watson, D. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 3663−3667. (f) Sunderhaus, J. D.; Lam, H.; Dudley, G. B. *Org. Lett.* **2003**, *5*, 4571−4573.

(7) (a) Malik, H. A.; Sormunen, G. J.; Montgomery, J. *J. Am. Chem. Soc.* **2010**, *132*, 6304−6305. (b) Liu, P.; Montgomery, J.; Houk, K. N. *J. Am. Chem. Soc.* **2011**, *133*, 6956−6959. (c) Li, W.; Chen, N.; Montgomery, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 8712−8716. (d) Negretti, S.; Narayan, A. R. H.; Chiou, K. C.; Kells, P. M.; Stachowski, J. L.; Hansen, D. A.; Podust, L. M.; Montgomery, J.; Sherman, D. H. *J. Am. Chem. Soc.* **2014**, *136*, 4901−4904. (e) Miller, Z. D.; Li, W.; Belderrain, T. R.; Montgomery, J. *J. Am. Chem. Soc.* **2013**, *135*, 15282−15285.

(8) (a) Boden, C. D. J.; Pattenden, G.; Ye, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2417−2419. (b) Uenishi, J.; Kawahama, R.; Yonemitsu, O. *J. Org. Chem.* **1996**, *61*, 5716−5717. (c) Maleczka, R. E.; Lavis, J. M.; Clark, D. H.; Gallagher, W. P. *Org. Lett.* **2000**, *2*, 3655−3658. (d) Luo, F.-T.; Hsieh, L.-C.; Fwu, S.-L.; Hwang, W.-S. *J. Chin. Chem. Soc.* **1994**, *41*, 605−607.

(9) (a) Takahashi, K.; Minami, T.; Ohara, Y.; Hiyama, T. *Tetrahedron Lett.* **1993**, *34*, 8263−8266. (b) Takahashi, K.; Minami, T.; Ohara, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2649−2656. (c) Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443−444. (d) Montenegro, J.; Bergueiro, J.; Saa, C.; Lopez, S. *Org. Lett.* **2009**, *11*, 141−144. (e) Denmark, S. E.; Wang, Z. *Org. Synth.* **2005**, *81*, 54−62. (f) Thiot, C.; Schmutz, M.; Wagner, A.; Mioskowski, C. *Chem.—Eur. J.* **2007**, *13*, 8971−8978. (g) Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073−1076. (h) Trost, B. M.; Machacek, M. R.; Ball, Z. T. *Org. Lett.* **2003**, *5*, 1895−1898. (i) Sore, H. F.; Blackwell, D. T.; MacDonald, S. J. F.; Spring, D. R. *Org. Lett.* **2010**, *12*, 2806−2809.

(10) (a) Gaillard, S.; Bantreil, X.; Slawin, A. M. Z.; Nolan, S. P. *Dalton Trans.* **2009**, 6967−6971. (b) For a description of the role of backbone substitution on ligand electronic properties, see: Van Ausdall, B. R.; Glass, J. L.; Wiggins, K. M.; Aarif, A. M.; Louie, J. *J. Org. Chem.* **2009**, *74*, 7935−7942.

(11) (a) Meiries, S.; Speck, K.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2013**, *32*, 330−339. (b) Nelson, D. J.; Collado, A.; Manzini, S.; Meiries, S.; Slawin, A. M. Z.; Cordes, D. B.; Nolan, S. P. *Organometallics* **2014**, *33*, 2048−2058.

(12) (a) Anderson, J. C.; Munday, R. *J. Org. Chem.* **2004**, *69*, 8971−8974. (b) Denmark, S. E.; Tymonko, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 8004−8005. (c) Denmark, S. E.; Christy, M. E. L.; Tymonko, S. A. *J. Org. Chem.* **2006**, *71*, 8500−8509.

(13) (a) Burks, H. E.; Liu, S. B.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 8766−8773. (b) Abe, Y.; Kuramoto, K.; Ehara, M.; Nakatsuji, H.; Suginome, M.; Murakami, M.; Ito, Y. *Organometallics* **2008**, *27*, 1736−1742.

(14) Xie, H. J.; Zhao, L. J.; Yang, L.; Lei, Q. F.; Fang, W. J.; Xiong, C. H. *J. Org. Chem.* **2014**, *79*, 4517−4527.