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Cobalt-Catalyzed Diborylation of 1,1-disubstituted Vinylarenes: A Practical Access to Branched *gem*-Bis(boryl)alkanes

Wei Jie Teo and Shaozhong Ge*

Abstract: We report the first catalytic diborylation of 1,1disubstituted vinylarenes with pinacolborane using a cobalt catalyst generated from bench-stable $Co(acac)_2$ and xantphos. A wide range of 1,1-disubstituted vinylarenes underwent this transformation to produce the corresponding *gem*-bis(boryl)alkanes in modest to high isolated yields. This cobalt-catalyzed protocol can be readily conducted on a gram scale without the use of a dry box and represents a practical and effective approach to access a wide range of branched *gem*-bis(boryl)alkanes.

Organoboronate compounds are synthetically valuable building blocks in organic synthesis due to their low toxicity and high functional-group compatibility.^[1] As an important class of organoboryl compounds, gem-bis(boryl)alkanes can undergo a wide range of organic transformations. For examples, the carboanions generated from gem-bis(boryl)alkanes in the presence of bases can selectively react with a variety of electrophiles, such as alkylhalides,^[2] *N*-heteroaromatic *N*-oxides,^[3] alkenes,^[4] and carbonyls.^[5] In addition, *gem*bis(boryl)alkanes can undergo various metal-catalyzed crosscoupling reactions, such as arylation $^{\rm [6]}$ and vinylation, $^{\rm [7]}$ allylic substitution,^[8] alkylation,^[9] epoxide ring-opening^[10] and 1,2addition of imines^[11] and carbonyl groups.^[12] Furthermore, the recent studies on sequential reactions using gembis(boryl)alkanes have highlighted their synthetic utilities as one of boryl groups remains intact after conversions of one boryl group.^[7a, 7c, 5c] Therefore, it is highly desirable to develop practical and atom-economic protocols, especially the ones that can address the limitations of current synthetic methodologies, for syntheses of gem-bis(boryl)alkanes from readily accessible starting materials.

Conventionally, *gem*-bis(boryl)alkanes can be prepared via the lithiation of bis(boryl)methane with LDA or Li(TMP) followed by the reactions with alkylhalides^[13] or the reactions of *gem*dihaloalkanes with B₂pin₂.^[14] However, the use of strong bases or limited availability of dibromo-analogues limits the scope of *gem*-bis(boryl)alkane products. Recently, Liu has reported a new approach to prepare *gem*-bis(boryl)alkanes through a baseinduced borylation of C-OBpin bonds in *α*-oxyboronate alkylboronates (RC(OBpin)Bpin) with B₂Pin₂.^[15] However, this borylation reaction requires boryl-pre-functionalized starting materials.

To develop more atom-economic approaches to prepare *gem*-bis(boryl)alkanes, catalytic dihydroboration of alkynes was studied and various transition metal catalysts based on Rh, Cu and Co have been developed (Scheme 1A).^[16] Alternatively,

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catalytic hydroboration of vinylboronates, which can be prepared by hydroboration of alkynes, also affords *gem*-bis(boryl)alkanes. For example, Hall and Yun developed a Cu-catalyzed asymmetric hydroboration of vinyl-Bdan with HBpin to prepare chiral *gem*-bis(boryl)alkanes (Scheme 1B).^[17] Very recently, Fu and Xiao have reported a Ni-catalyzed diborylation of alkenes with B₂pin₂ in the presence of bases at 130 °C, but only monosubstituted alkenes undergo this Ni-catalyzed diborylation (Scheme 1C).^[18] However, *gem*-bis(boryl)alkanes prepared by these catalytic dihydroboration or diborylation reactions of alkynes or alkenes are limited to the ones with methylene groups at the β -position.



Scheme 1. Catalytic protocols for the synthesis of gem-bis(boryl)alkanes.

Diborylation of methylene C-H bonds has also been developed to prepare *gem*-bis(boryl)alkanes,^[19] but the bis(boryl) products were limited to 1,1-benzyldiboronates. Very recently, Chirik reported a Co-catalyzed diborylation of non-benzylic C-H bonds in branched alkylarenes to access *gem*-bis(boryl)alkanes containing a branched alkyl group (Scheme 1D).^[19b] However, this transformation requires very high catalyst loading and copious amounts of boron reagents, and the desired *gem*-bis(boryl)alkanes, we are interested in develop a selective and efficient protocol to synthesize *gem*-bis(boryl) compounds containing branched alkyl groups through a Co-catalyzed diborylation of 1,1-disubstituted vinylarenes with pinacolborane (Scheme 1E).

Recently, cobalt complexes have been emerging as active catalysts for hydroboration^[20] and dehydrogenative borylation reactions^[21] of alkenes or alkynes to prepare organoboron compounds with one or multiple boryl groups. During our studies on the Co-catalyzed hydrofunctionalization of unsaturated hydrocarbons,^[21f,22] we found that the reaction of α -methylstyrene with HBpin in the presence of Co(acac)₂ and xantphos afforded the hydroboration product **1a**, together with

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an unexpected *gem*-bis(boryl) product **2a** (eq 1). In this reaction, 40% of α -methylstyrene was sacrificed and concomitantly hydrogenated to cumene. In order to develop this reaction into a selective protocol for the synthesis of gem-bis(boryl) compounds, we tested various alkenes as hydrogen acceptors and cobalt catalysts generated from Co(acac)₂ and various bisphosphine ligands for this transformation. The selected experiments are summarized in Table 1.



This hydroboration reaction catalyzed by Co(acac)₂/xantphos in the presence of 1.2 equivalent of norbornene afforded the desired bis(boryl)alkene 2a in 88% yield with an excellent chemoselectivity (96% for 2a, entry 1 in Table 1). Decreasing the amount of norbornene to 1 equivalent resulted in a decreased selectivity to 2a (entry 2 in Table 1). Similarly high yield and selectivity for 2a were obtained for this reaction when norbornadiene was used as a hydrogen acceptor (entry 3 in Table 1). When other alkenes, such as cyclohexene, tertbutylethylene, or 3-ethyl-2-pentene, were used as hydrogen acceptors, this reaction showed significantly lower selectivity for 2a (entries 4-6 in Table 1). However, when catalyzed by the combination of Co(acac)₂ and other bisphosphine ligands, such as dppe, dcpe, dppp, dppbz, or dpephos, these reactions afforded the hydroboration product 1a together with 2norbornylboronate as major products and only small amounts of product 2a were detected (entries 7-11 in Table 1).

Table 1. Evaluation of conditions for Co-catalyzed diborylation of $\alpha\text{-}$ methylstyrene with pinacolborane^{[a]}

\sim	Me + HBpin	Co(acac)2 (2 mol %) ligand (2 mol %) hydrogen acceptor (1.2 equiv.)		Bpin Bpin	Bpin
\bigcirc		THF, 50 °C,		19	20
entry	ligand	hydrogen acceptor	Conversion (%) ^[b]	Yield of 2a (%) ^[b]	1a:2a ^[b]
1	xantphos	norbornene (nbe)	>99	88	4:96
2	xantphos	nbe (1 equiv.)	>99	74	12:88
3	xantphos	norborndiene	>99	83	5:95
4	xantphos	cyclohexene	>99	63	24:76
5	xantphos	tert-butylethylene	>99	47	16:84
6	xantphos	3-ethyl-2-pentene	>99	39	34:66
7	dppe	nbe	20	<5	94:6
8	dcpe	nbe	24	<5	97:3
9	dppp	nbe	38	10	70:30
10	dppbz	nbe	55	<5	99:1
11	dpephos	nbe	32	22	15:85
P	Me Me O Ph ₂ PPh ₂ xantphos	Cy ₂ P PCy ₂ Ph ₂ P PPh ₂ Ph ₂ P PPh	2 dcpe 2 dppe	PPh ₂ PPh ₂ bz dpept	PPh ₂ nos

[a] Conditions: α -methylstyrene (0.250 mmol), pinacoborane (0.525 mmol), Co(acac)₂ (5.0 µmol), ligand (5.0 µmol), hydrogen acceptor (0.300 mmol), THF (1 mL), 50 °C, 12 h; ^bThe conversion of α -methylstyrene, yield of **2a**, and the ratios of **1a:2a** were determined with gas chromatography (GC) analysis with dodecane as an internal standard.

Under the identified conditions (entry 1 in Table 1), we studied the scope of 1,1-disubstituted vinylarenes that undergo this cobalt-catalyzed bisborylation reaction and the results are summarized in Table 2. In general, a wide range of α -methyl-

substituted vinylarenes containing electronically varied aryl groups reacted smoothly at 50 °C, yielding the corresponding gem-bis(boryl)alkenes (2a-2r) in modest to high isolated yields (55-87%).^[23] The GC-MS analysis on the crude mixtures of these reactions indicated the formation of trace amounts (< 5%) of hydroboration products and iso-propylarenes that were generated by hydrogenation of α -methyl vinylarenes. In addition, we also tested vinylarene with various aliphatic substituents at the α -position for this transformation. These vinylarenes containing sterically varied linear (2s-2aa) or cyclic (2ab-2af) aliphatic groups also reacted smoothly to produce the desired bis(boryl) compounds (2s-2af), albeit in modest yields. This cobalt-catalyzed bisborylation reaction of vinylarenes tolerates various functionalities, including ether (2b-2d, 2f, 2i, 2ac, and 2af), thioether (2j), siloxy (2q and 2z), chloro (2m), tertiary amine (2k and 2x), chloro (2m), sulfonyl (2o), acetal (2r), carboxylic ester (2y), pinacolboryl (2aa), and carbamate (2ae and 2af) moieties. Ketone, and free hydroxyl groups are incompatible with the reaction conditions. However, vinylarenes containing a ketone (2r) protected as acetal and an alcohol (2q and 2z) protected as silvl ether reacted to afford the corresponding bis(boryl) product in good yields.

Table 2. Scope of 1,1-disubstituted vinylarenes^[a]





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After establishing the scope of this bisborylation reaction, we subsequently demonstrated synthetic utilities of this protocol (Scheme 2). First, we tested a gram scale reaction of 1methylene-1,2,3,4-tetrahydronaphthalene and HBpin with Co(acac)₂ and xantphos weighed on bench top, and this reaction proceeded smoothly under the developed conditions to produce product 2ab in 54% isolated yield (Scheme 2A). Bis(boryl)alkane 2ab was oxidized with NaBO₃ to form an aldehyde 3 in 59% yield (Scheme 2B), which provides a facile pathway to achieve aldehydes through functionalization of alkenes. This bis(boryl)alkane 2ab also underwent a boron-Wittig reaction with an aldehyde to afford ketone 4 in 65% isolated yield (Scheme 2C). Furthermore, Suzuki-Miyaura cross-coupling between 2ab and 4-iodoanisole occurred in a diastereoselective fashion in the presence of 5 mol% of Pd(P^tBu₃)₂, affording a benzyl boronate 5 with a high diastereoselectivity (dr > 20:1), albeit in a modest isolated yield (Scheme 2D).



Scheme 2. Synthetic utilities of this cobalt-catalyzed bis(borylation) reaction.



Scheme 3. Deuterium-labelling experiments

To provide insights into the reaction mechanism, we conducted a series of deuterium-labelling experiments (Scheme 3). The bisborylation reaction of α -ethyl-4-*tert*-butyl-styrene with DBpin under standard conditions afforded the desired *gem*-bis(boryl)alkane **2ag** in 51% isolated yield (Scheme 3A). However, no deuterium incorporation into **2ag** was detected by the ²H NMR analysis. Instead, GC-MS analysis indicated the

formation of norbornane- d_2 . Subsequently, we conducted this bisborylation reaction with α -ethyl-4-*tert*-butyl-styrene- d_2 and HBpin and found that both deuterium atoms were retained in the product **2ag**- d_2 , but with one deuterium shifted from terminal vinylic carbon to the benzylic carbon of **2ag** (Scheme 3B). Furthermore, we conducted a crossover experiment using a 1:1 mixture of α -ethyl-4-*tert*-butyl-styrene- d_2 and α -methylstyene, and found that this reaction did not afford any H/D-scrambled products (Scheme 3C). The result of this crossover experiment suggests that the deuterium shift observed in Scheme 3B occurred intramolecularly.

Based on the results of deuterium labelling experiments and precedent of cobalt-catalyzed hydroboration the and borylation reactions of alkenes,^[20,21] dehydrogenative we proposed a possible catalytic cycle for this Co-catalyzed bisborylation reaction (Scheme 4A). Activation of Co(acac)₂ with HBpin in the presence of a bisphosphine ligand generates a Co(I)-H species, [21c,24] which turns into a Co(I)-Bpin species by the reaction with norbornene and HBpin through intermediate I-A.^[25] Subsequently, 2,1-migratory insertion of a vinylarene with this Co(I)-Bpin species forms a sterically hindered alkylcobalt intermediate I-B, which undergoes valence tautomerization to less hindered alkylcobalt species I-C through a cyclic σ , π transition state.^[26] The alkylcobalt I-C then turns over with HBpin to afford the bis(boryl)alkane product and regenerates the Co(I)-H species. To gain further support for this pathway, we rationalize that the allylboronate 6 can undergo migratory insertion into a Co(I)-H species to form the alkylcobalt intermediate I-B, which reacts with HBpin and releases the product 2a (Scheme 4B). Indeed, the hydroboration of the alkylboronate with HBpin catalyzed by Co(acac)₂/xantphos occurred smoothly to afforded the gem-bis(boryl)alkane 2a in 51% yield (Scheme 4C).



Scheme 4. Proposed catalytic pathway for the cobalt-catalyzed diborylation of 1,1-disubstituted vinylarenes

Alternatively, the alkylcobalt **I-B** can undergo β –H elimination to form a vinylboronate and a Co(I)-H species and subsequent insertion of the vinylboronate into this Co(I)-H species generates

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the alkylcobalt species I-C [eq (2)]. To test this possibility, we conducted reactions of a vinylboronate **7** with HBpin catalyzed by $Co(acac)_2$ /xantphos in the presence or in the absence of norbornene, and found that the desired bis(boryl)alkane product **2a** was not formed under both sets of conditions [eq (3)]. The results of these experiments suggest that vinylboronates are not intermediates for this diborylation reaction, which is in contrast to the triborylation reaction of styrenes to form alkyltriboronates.^[21a]



In summary, we have developed a convenient and efficient protocol for the synthesis of *gem*-bis(boryl)alkanes through a catalytic diborylation of 1,1-disubstituted vinylarenes with pinacolborane using a cobalt catalyst generated in situ from bench stable $Co(acac)_2$ and xantphos. A variety of sterically and electronically varied vinylarenes reacted to afford *gem*-bis(boryl) products in good isolated yields. In addition, this reaction can be conducted on a gram scale without the use of a dry box. Further studies on details of the reaction mechanism and the development of an asymmetric version of this reaction are the subjects of future work.

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Keywords: cobalt • diborylation • vinylarene • homogeneous catalysis • *gem*-bis(boryl)alkane

- a) R. M. Adams, Boron, metallo-boron compounds, and boranes, Interscience Publishers, 1964; b) S. E. Thomas, Organic Synthesis, the Roles of Boron and Silicon, 1991; c) N. Miyaura, A. Suzuki, Chem. Rev. 1995, 95, 2457; d) M. Norio, Bull. Chem. Soc. Jpn. 2008, 81, 1535; e) E. Fernández, A. Whiting, Synthesis and Application of Organoboron Compounds, Springer International Publishing, 2015.
- [2] K. Hong, X. Liu, J. P. Morken, J. Am. Chem. Soc. 2014, 136, 10581.
- [3] a) W. Jo, J. Kim, S. Choi, S. H. Cho, Angew. Chem. Int. Ed. 2016, 55, 9690; b) C. Hwang, W. Jo, S. H. Cho, Chem. Commun. 2017, 53, 7573.
- [4] X. Liu, T. M. Deaton, F. Haeffner, J. P. Morken, Angew. Chem. Int. Ed. 2017, 56, 11485.
- [5] a) J. R. Coombs, L. Zhang, J. P. Morken, *Org. Lett.* **2015**, *17*, 1708; b)
 J. Park, S. Choi, Y. Lee, S. H. Cho, *Org. Lett.* **2017**, *19*, 4054; c) T. C. Stephens, G. Pattison, *Org. Lett.* **2017**, *19*, 3498.
- [6] a) K. Endo, T. Ohkubo, M. Hirokami, T. Shibata, J. Am. Chem. Soc.
 2010, 132, 11033; b) K. Endo, T. Ohkubo, T. Shibata, Org. Lett. 2011, 13, 3368; c) C. Sun, B. Potter, J. P. Morken, J. Am. Chem. Soc. 2014, 136, 6534; d) H. Y. Sun, K. Kubota, D. G. Hall, Chem. Eur. J. 2015, 21, 19186; e) S. Xu, X. Shangguan, H. Li, Y. Zhang, J. Wang, J. Org. Chem. 2015, 80, 7779.
- [7] a) H. Li, Z. Zhang, X. Shangguan, S. Huang, J. Chen, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2014**, 53, 11921; b) B. Potter, A. A. Szymaniak, E. K. Edelstein, J. P. Morken, *J. Am. Chem. Soc.* **2014**, 136, 17918; c) B. Potter, E. K. Edelstein, J. P. Morken, *Org. Lett.* **2016**, 18, 3286.

- [8] J. Kim, S. Park, J. Park, S. H. Cho, Angew. Chem. Int. Ed. 2016, 55, 1498.
- a) K. Endo, T. Ohkubo, T. Ishioka, T. Shibata, *J. Org. Chem.* 2012, *77*, 4826; b) Z.-Q. Zhang, C.-T. Yang, L.-J. Liang, B. Xiao, X. Lu, J.-H. Liu, Y.-Y. Sun, T. B. Marder, Y. Fu, *Org. Lett.* 2014, *16*, 6342; c) F. Li, Z.-Q. Zhang, X. Lu, B. Xiao, Y. Fu, *Chem. Commun.* 2017, *53*, 3551.
- [10] a) A. Ebrahim-Alkhalil, Z.-Q. Zhang, T.-J. Gong, W. Su, X.-Y. Lu, B. Xiao, Y. Fu, *Chem. Commun.* **2016**, *52*, 4891; b) S. A. Murray, M. Z. Liang, S. J. Meek, *J. Am. Chem. Soc.* **2017**, *139*, 14061.
- [11] a) J. Park, Y. Lee, J. Kim, S. H. Cho, Org. Lett. 2016, 18, 1210; b) J. Kim, K. Ko, S. H. Cho, Angew. Chem. Int. Ed. 2017, 56, 11584.
- [12] a) M. V. Joannou, B. S. Moyer, M. J. Goldfogel, S. J. Meek, Angew. Chem. Int. Ed. 2015, 54, 14141; b) M. V. Joannou, B. S. Moyer, S. J. Meek, J. Am. Chem. Soc. 2015, 137, 6176; c) S. A. Murray, J. C. Green, S. B. Tailor, S. J. Meek, Angew. Chem. Int. Ed. 2016, 55, 9065.
- [13] D. S. Matteson, R. J. Moody, *Organometallics* **1982**, *1*, 20.
- [14] a) T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu, T. Hiyama, Angew. Chem. Int. Ed. 2001, 40, 790; b) T. Kurahashi, T. Hata, H. Masai, H. Kitagawa, M. Shimizu, T. Hiyama, Tetrahedron 2002, 58, 6381; c) S. Masaki, S. Michael, N. Ikuhiro, S. Katsuhiro, K. Takuya, H. Tamejiro, Chem. Lett. 2006, 35, 1222.
- [15] L. Wang, T. Zhang, W. Sun, Z. He, C. Xia, Y. Lan, C. Liu, J. Am. Chem. Soc. 2017, 139, 5257.
- [16] a) K. Endo, M. Hirokami, T. Shibata, *Synlett.* 2009, 2009, 1331; b) S.
 Lee, D. Li, J. Yun, *Chem. Asian J.* 2014, *9*, 2440; c) Z. Zuo, Z. Huang, *Org. Chem. Front.* 2016, *3*, 434.
- [17] a) J. C. H. Lee, R. McDonald, D. G. Hall, *Nat. Chem.* 2011, *3*, 894; b) X.
 Feng, H. Jeon, J. Yun, *Angew. Chem., Int. Ed.* 2013, *52*, 3989.
- [18] L. Li, T. Gong, X. Lu, B. Xiao, Y. Fu, Nat. Commun. 2017, 8, 345.
- [19] a) S. H. Cho, J. F. Hartwig, *Chem. Sci.* 2014, *5*, 694; b) W. N. Palmer,
 J. V. Obligacion, I. Pappas, P. J. Chirik, *J. Am. Chem. Soc.* 2016, *138*,
 766; c) W. N. Palmer, C. Zarate, P. J. Chirik, *J. Am. Chem. Soc.* 2017,
 139, 2589.
- [20] For recent examples: a) J. V. Obligacion, P. J. Chirik, J. Am. Chem. Soc. 2013, 135, 19107; b) L. Zhang, Z. Zuo, X. Leng, Z. Huang, Angew. Chem., Int. Ed. 2014, 53, 2696; c) L. Zhang, Z. Zuo, X. Wan, Z. Huang, J. Am. Chem. Soc. 2014, 136, 15501; d) J. V. Obligacion, J. M. Neely, A. N. Yazdani, I. Pappas, P. J. Chirik, J. Am. Chem. Soc. 2015, 137, 5855; e) W. N. Palmer, T. Diao, I. Pappas, P. J. Chirik, ACS Catal. 2015, 5, 622; f) H. Zhang, Z. Lu, ACS Catal. 2016, 6, 6596; g) T. Xi, Z. Lu, ACS Catal. 2017, 7, 1181; h) J. Peng, J. H. Docherty, A. P. Dominey, S. P. Thomas, Chem. Commun. 2017, 53, 4726; i) A. D. Ibrahim, S. W. Entsminger, A. R. Fout, ACS Catal. 2017, 7, 3730; j) S. Krautwald, M. J. Bezdek, P. J. Chirik, J. Am. Chem. Soc. 2017, 139, 3868.
- [21] a) L. Zhang, Z. Huang, J. Am. Chem. Soc. 2015, 137, 15600; b) H.
 Wen, L. Zhang, S. Zhu, G. Liu, Z. Huang, ACS Catal. 2017, 7, 6419.
 For recent examples of dehydrogenative borylation of alkenes by other transition metal catalysts, see: c) T. Ohmura, Y. Takasaki, H. Furukawa, M. Suginome, Angew. Chem., Int. Ed. 2009, 48, 2372; d) J. Takaya, N.
 Kirai, N. Iwasawa, J. Am. Chem. Soc. 2011, 133, 12980; e) M.
 Morimoto, T. Miura, M. Murakami, Angew. Chem., Int. Ed. 2015, 54, 12659; f) C. Wang, W. J. Teo, S. Ge, ACS Catal. 2017, 7, 855.
- [22] a) W. J. Teo, C. Wang, Y. W. Tan, S. Ge, Angew. Chem., Int. Ed. 2017, 56, 4328; b) S. Yu, C. Wu, S. Ge, J. Am. Chem. Soc. 2017, 139, 6526.
- [23] CCDC 1578773 (2K) contains the supplementary crystallographic data for this manuscript. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.
- [24] For additional examples of the reduction of Co(II) precursors to Co(I) species, see: a) Y. Ohki, Y. Shimizu, R. Araake, M. Tada, W. M. C. Sameera, J.-I. Ito, H. Nishiyama, *Angew. Chem. Int. Ed.* **2016**, *55*, 15821; b) Y. Liu, L. Deng, *J. Am. Chem. Soc.* **2017**, *139*, 1798.
- [25] Compared with cobalt catalysts containing a sterically less hindered biphosphine ligand (dppe, dppp, or dppbz, see Table 1), the large bite angle of xantphos plays a significant role in the formation of a Co-Bpin species.
- [26] G. N. Schrauzer, J. H. Weber, T. M. Beckham, J. Am. Chem. Soc. 1970, 92, 7078.

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Alkene Diborylation: A highly chemoselective cobalt-catalyzed diboration of 1,1disubstituted vinylarenes with pinacolborane has been developed using a catalyst generated from bench-stable Co(acac)₂ and xantphos (see the Picture). A wide range of α -vinylarenes reacted to afford the corresponding branched *gem*bis(boryl)alkanes in high isolated yields. Wei Jie Teo and Shaozhong Ge*

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