

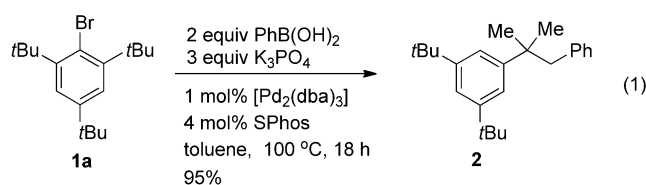
C–H Amination

Palladium(0)-Catalyzed Intermolecular Amination of Unactivated C_{sp}³–H Bonds**

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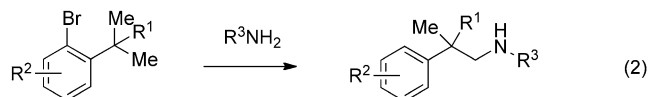
Nitrogen-containing compounds are ubiquitous among biologically active molecules.^[1] Consequently, the development of efficient methods to form carbon–nitrogen bonds is of great importance. From a synthetic standpoint, a strategy involving transition-metal-catalyzed C–H bond activation followed by C–N bond formation represents an extremely attractive approach for installing nitrogen functional groups.^[2] In fact, great achievements have been made based on amination of C_{sp}²–H bonds,^[3] as well as activated C_{sp}³–H bonds.^[3h,4] However, the activation of a simple C_{sp}³–H bond followed by C–N bond formation remains a challenge, especially in an intermolecular fashion.^[5] To the best of our knowledge, the intermolecular C–H amination of unactivated C_{sp}³–H bonds has only been reported using in situ generated, highly reactive nitrene intermediates.^[6] Thus, the development of complementary methods is strongly desired. Herein, we report on the palladium(0)-catalyzed intermolecular C–H amination of unactivated C_{sp}³–H bonds using aryl amines as the nitrogen source.

During our investigation of Suzuki–Miyaura cross-coupling processes,^[7] we disclosed that the reaction of 1-bromo-2,4,6-tri-*tert*-butylbenzene (**1a**) with phenylboronic acid produced the α,α -dimethyl- β -phenyl hydrostyrene, **2**, in 95% yield, instead of the desired biaryl [Eq. (1); dba = dibenzylideneacetone]. This transformation likely proceeds by a pathway involving a tandem C–H activation/Suzuki–Miyaura cross-coupling reaction. On the basis of these results, we postulated that a related transformation involving an intermolecular tandem C_{sp}³–H activation/C–N coupling might be feasible [Eq. (2)].



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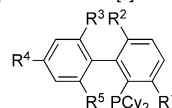


Our study commenced by examining the C–H amination of **1a** to afford the corresponding *N*-(2-methyl-2-phenylpropyl)aniline, **3a**, using palladium catalysts having different ligands. While the biarylphosphane ligands developed in our laboratory led to catalysts that exhibited modest activities (Table 1, entries 1–7),^[8] an examination of alternative ligand classes revealed that the utilization of an *N*-heterocyclic carbene ligand (SIPr-HBF₄) provided a significantly improved reaction efficiency to afford **3a** in 80% yield

Table 1: Ligand evaluation.^[a,b]

Entry	Ligand	Yield [%] ^[e]	Entry	Ligand	Yield [%] ^[e]
1	XPhos	30	8 ^[c]	PCy ₃ ·HBF ₄	0
2	SPhos	23	9 ^[c]	PtBu ₃ ·HBF ₄	59
3	RuPhos	32	10 ^[c]	IMes·HCl	0
4	DavePhos	7	11 ^[c]	IPr·HCl	30 ^[f]
5	CPhos	23	12 ^[c]	SIPr·HCl	72
6	BrettPhos	0	13 ^[c]	SIPr-HBF ₄	86 (80)
7	Cy-JohnPhos	0	14 ^[d]	SIPr-HBF ₄	88 (83)

[a] Reaction conditions: **1a** (0.5 mmol), PhNH₂ (0.6 mmol), NaOtBu (0.75 mmol), [Pd₂(dba)₃] (5 mol %), ligand (20 mol %), dioxane (5 mL), 120 °C, 40 h. [b] The reaction reached 100% conversion, unless otherwise noted. The mass balance consists of product, reduced starting material, and benzocyclobutene by-product. [c] Reaction was run at 110 °C for 12 h. [d] Reaction was performed in toluene with 11 mol % ligand at 110 °C for 4 h. [e] Determined by GC, with dodecane as an internal standard. Yield of isolated **3a** (1 mmol scale reaction) in parentheses. [f] The reaction reached 58% conversion.



XPhos: R¹=R²=H, R³=R⁴=R⁵=*i*Pr

SPhos: R¹=R²=R⁴=H, R³=R⁵=OMe

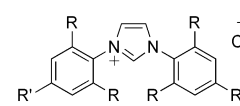
RuPhos: R¹=R²=R⁴=H, R³=R⁵=O/*i*Pr

DavePhos: R¹=R²=R³=R⁴=H, R⁵=NMe₂

CPhos: R¹=R²=R⁴=H, R³=R⁵=NMe₂

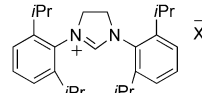
BrettPhos: R¹=R²=OMe, R³=R⁴=R⁵=*i*Pr

Cy-JohnPhos: R¹=R²=R³=R⁴=R⁵=H



IMes HCl: R=R'=Me

IPr HCl: R=*i*Pr, R'=H



SIPr HCl: X=Cl

SIPr-HBF₄: X=BF₄

(Table 1, entry 13).^[9] Further optimization of the solvent system led to an 83 % yield of the isolated **3a** (Table 1, entry 14).

With optimized reaction conditions in hand, we then evaluated the scope of the C–H amination of **1a** with respect to the aryl amine component (Table 2). Both electron-rich and electron-deficient anilines gave the expected products in good to excellent yield (**3a–3f**), as well as anilines containing an *ortho*-alkyl substituent (**3e**). We were pleased to find that heteroaryl amines such as 3-aminopyridine and 3-aminquinoline also provided the corresponding products in good yields (**3g**, **3h**). Unfortunately, *N*-substituted anilines and alkyl amines do not work under the current reaction conditions. Notably, for reactions of **1a** with aryl amines, no diaryl amines were observed despite the fact that SIPr-HBF₄ is an efficient ligand for palladium-catalyzed C–N cross-coupling reactions.^[10] We reasoned that this was likely due to the steric effects of the two *ortho* *tert*-butyl groups of **1a**.

We next examined the reactivity of less sterically hindered substrates (Table 3). The reaction of **4a** with aniline produced the diaryl amine **4b** as the sole product (Table 3, entry 1). It is likely that the *ortho*-methyl group does not possess the steric bulk necessary to suppress the direct C–N cross-coupling. Replacing the methyl group with a bulkier isopropyl, cyclopentyl, or cyclohexyl group led to complete suppression of the C–N cross-coupling pathway, thus affording the desired C–H amination products exclusively in 75–81 % yields (Table 3, entries 2–4). No C–H amination of the isopropyl, cyclopentyl,

Table 2: C–H amination of **1a** with aryl amines.^[a]

Product	Yield [%] ^[b]	Product	Yield [%] ^[b]
	83		76
	84		76
	86		75
	73		84

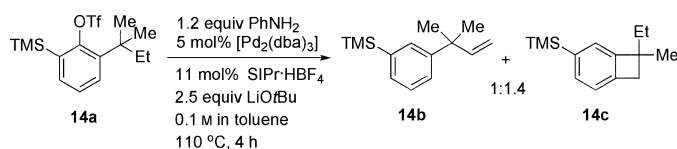
[a] Reaction conditions: **1a** (1.0 mmol), ArNH₂ (1.2 mmol), NaOtBu (1.5 mmol), [Pd₂(dba)₃] (5 mol %), SIPr-HBF₄ (11 mol %), toluene (10 mL), 110 °C, 4 h. [b] Yield of isolated product is based on an average of two runs.

Table 3: Amination of unactivated C_{sp}³–H bonds with aniline.^[a]

Entry	Substrate	Product	Yield [%] ^[b]
1			94
2			75
3			77
4			81
5			82
6			40
			41
7			70
8			80
9 ^[c]			70
			37
10 ^[c]			35

[a] Reaction conditions: substrate (1.0 mmol), PhNH₂ (1.2 mmol), NaOtBu (1.5 mmol), [Pd₂(dba)₃] (5 mol %), SIPr-HBF₄ (11 mol %), toluene (10 mL), 110 °C, 4 h. [b] Yield of isolated product is based on an average of two runs. [c] LiOtBu (2.5 mmol) was used. Tf = trifluoromethanesulfonyl, TIPS = triisopropylsilyl, TMS = trimethylsilyl.

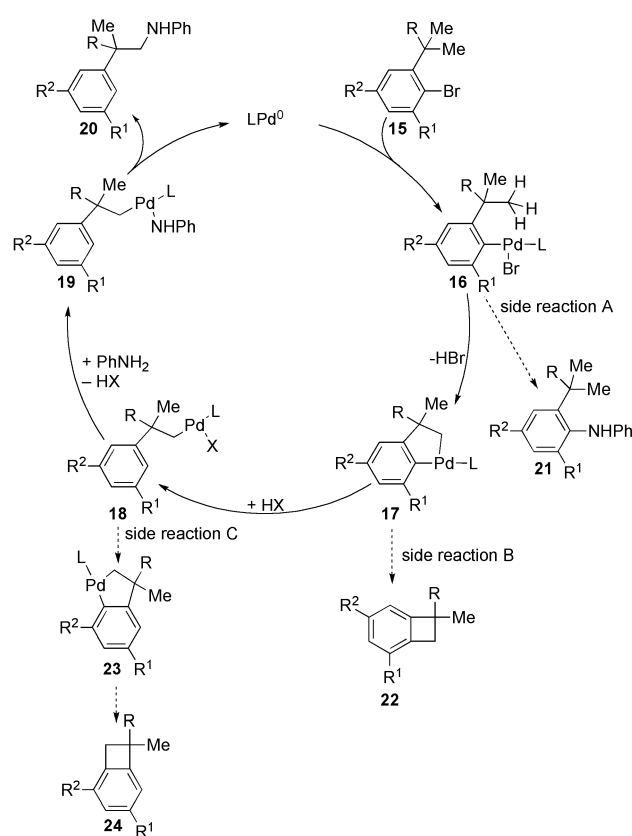
or cyclohexyl group was observed, thereby indicating that the amination is highly selective for only the methyl groups of the *tert*-butyl group. The steric influence on the outcome of this reaction could be further illustrated when using the diol-protected benzaldehyde substrates **8a**, **9a**, and **10a**. In the reaction of the ethylene-glycol-protected substrate **8a** with aniline, only the direct C–N cross-coupling product **8b** was observed (Table 3, entry 5). However, using a more sterically hindered pinacol protecting group led to the formation of a 1:1 ratio of the C–N cross-coupling product **9b** and the C–H amination product **9c** (Table 3, entry 6). An additional increase in size of the diol protecting group resulted in exclusive formation of the C–H amination product **10b** (Table 3, entry 7). Thus, a simple switch of the diol from ethylene glycol to 2,4-dimethyl-2,4-pentanediol allows access to both the C–N cross-coupling product and the C–H amination product selectively. In addition, substrate **11a** bearing an *ortho*-OTIPS group underwent the C–H amination smoothly giving the desired product **11b** in 80% yield (Table 3, entry 8). Notably, the reaction was not restricted to aryl bromide substrates. Starting from aryl triflate **12a**, the corresponding C–H amination product **12b** was also produced in good yield when LiOtBu was employed as base instead of NaOtBu (Table 3, entry 9). C–H amination of the TMS group was not observed. Employing **13a** under the optimized reaction conditions provided the desired product **13b** along with the olefin product **13c** (Table 3, entry 10). The by-product **13c** possibly arose from the C–H activation of the ethyl group followed by β -hydride elimination.^[11] Interestingly, the *tert*-amyl group in the *para* position plays a crucial role in producing the desired product, as **14a** failed to yield any C–H amination product under the same reaction conditions. Instead, a mixture of olefin **14b** and benzocyclobutene **14c**^[12] was obtained in a ratio of 1:1.4 and in an 81% combined yield (Scheme 1). It is worth noting that the reactive benzylic and ethereal hydrogen atoms are tolerated



Scheme 1. Reaction of **14a** with aniline.

in the reaction (Table 3, entries 1–7). Therefore, it provides an orthogonal approach to the existing nitrene methods.^[2]

Based on the results described above, we propose a reaction mechanism as shown in Scheme 2. The oxidative addition of Pd⁰ to aryl bromide **15** gives intermediate **16**, which would undergo C–H activation of one of the C_{sp}³–H bonds to form the palladacycle **17**. Protonation of the C_{sp}²–Pd bond of **17** affords the alkyl Pd^{II} species **18**, which then undergoes transmetalation with aniline to give **19**. Finally, reductive elimination occurs to yield the product **20** with concomitant regeneration of LPd⁰. A sterically hindered R¹ group helps to suppress the direct C–N



Scheme 2. Proposed mechanism of the tandem C–H activation/C–N cross-coupling.

cross-coupling (side reaction A), as well as the benzocyclobutene formation (side reaction B).^[12] Therefore, it diminishes the formation of the undesired by-products **21** and **22**. In addition, as suggested by the results of the reaction of **14a** with aniline, a bulky R² group seems critical for minimizing the formation of the by-product **24** that most likely arises from the intramolecular C_{sp}²–H activation of **18** followed by reductive elimination (side reaction C).^[12]

To gain additional insight into the steric influence of the substrates **8a**, **9a**, and **10a** on direct C–N cross-coupling versus C–H amination, we performed a computational study at the density functional theory (DFT) level with the hybrid functionals B3LYP.^[13] The oxidative addition intermediates of **8a**, **9a**, and **10a** were evaluated (Table 4). The

Table 4: DFT calculations of the oxidative addition intermediates.

	OA1a	OA2a	OA3a
	2.962 Å	2.480 Å	2.277 Å
	134.7°	119.4°	116.9°

intermediates (**OA1a**, **OA2a**, and **OA3a**) with the carbene ligand trans to the aromatic ring are found to be more stable. The calculated distances between the Pd^{II} atom and the C–H σ bond of the *tert*-butyl group and the bond angles, Pd–C1–C2, are listed in Table 4. Notably, the distance decreases as the size of diol protecting group increases; that is, the Pd is being “pushed” toward the *tert*-butyl group as indicated by the decrease in the bond angle. In addition, the calculated distances are consistent with a three-center two-electron, agostic interaction between the Pd^{II} atom and the C–H σ bond in **OA2a** and **OA3a**.^[12,14] As recently demonstrated,^[14c,15] an agostic interaction increases the acidity of the C–H bond that is geminal to the agostic C–H bond. This increase in acidity is supported by the computed natural atomic charges. For **OA3a**, the agostic hydrogen atom has a less positive charge (+0.203) than either of the geminal hydrogen atoms (+0.227 and +0.225). Similar results were found for **OA2a** (agostic H: +0.150; geminal H: +0.209, 0.211). The shorter distance in **OA3a** suggests that the agostic interaction is likely stronger than that in **OA2a**. This stronger agostic interaction in **OA3** confers a more acidic character on the geminal hydrogen atom to be deprotonated. Consequently, the tendency for the subsequent C–H activation rises from **OA1a** to **OA3a** (**OA1a** < **OA2a** < **OA3a**), which is indeed consistent with our experimental observations.

In summary, we have developed a conceptually novel palladium(0)-catalyzed intermolecular C–H amination of unactivated C_{sp}³–H bonds using aryl amines as the nitrogen source. We have also demonstrated selective access to both the C–N cross-coupling product and the C–H amination product by adjusting the steric environment of the substrate. To the best of our knowledge, this reaction is the first intermolecular unactivated C_{sp}³–H bond activation/C–N bond-forming process that does not involve nitrenes. Additional investigations to increase the generality of this process and to better understand its mechanism are currently underway in our laboratory.

Experimental Section

Typical procedure: In a nitrogen-filled glovebox, aryl bromide (1.0 mmol, 1.0 equiv), [Pd₂(dba)₃] (46 mg, 5 mol %), SIPr-HBF₄ (53 mg, 11 mol %), NaOtBu (144 mg, 1.5 mmol, 1.5 equiv), aryl amine (1.2 mmol, 1.2 equiv), and toluene (10 mL) were added to an oven-dried test tube containing a magnetic stir bar. The test tube was sealed with a Teflon-lined septum, removed from the glovebox, and heated at 110 °C in a preheated oil bath for 4 h. After the reaction was complete, the reaction mixture was cooled to room temperature, filtered through a plug of silica gel, and eluted with diethyl ether. The filtrate was concentrated in vacuo and the crude product was purified by flash chromatography on silica gel (see the Supporting Information for details).

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- [1] a) C. Kibayashi, *Chem. Pharm. Bull.* **2005**, *53*, 1375; b) J. H. Cheng, K. Kamiya, I. Kodama, *Cardiovasc. Drug Rev.* **2001**, *19*, 152; c) C. Sanchez, C. Mendez, J. A. Salas, *Nat. Prod. Rep.* **2006**, *23*, 1007.
- [2] For recent reviews on C–H amination, see: a) A. Armstrong, J. C. Collins, *Angew. Chem.* **2010**, *122*, 2332; *Angew. Chem. Int. Ed.* **2010**, *49*, 2282; b) P. Thansandote, M. Lautens, *Chem. Eur. J.* **2009**, *15*, 5874; c) F. Collet, R. H. Dodd, P. Dauban, *Chem. Commun.* **2009**, 5061; d) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417; e) A. R. Dick, M. S. Sanford, *Tetrahedron* **2006**, *62*, 2439; f) H. M. L. Davies, M. S. Long, *Angew. Chem.* **2005**, *117*, 3584; *Angew. Chem. Int. Ed.* **2005**, *44*, 3518; g) P. Muller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905; h) F. Collet, C. Lescot, P. Dauban, *Chem. Soc. Rev.* **2011**, *40*, 1926; i) D. N. Zalatan, J. Du Bois, *Top. Curr. Chem.* **2010**, *292*, 347.
- [3] For selected examples of C–N bond formation following activation of C_{sp}³–H bonds, see: a) K. Sun, Y. Li, T. Xiong, J. Zhang, Q. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 1694; b) B. Xiao, T.-J. Gong, J. Xu, Z.-J. Liu, L. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 1466; c) Y. C. Tan, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 3676; d) K. H. Ng, A. S. C. Chan, W. Y. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 12862; e) K. Inamoto, T. Saito, K. Hiroya, T. Doi, *J. Org. Chem.* **2010**, *75*, 3900; f) D. Monguchi, T. Fujiwara, H. Furukawa, A. Mori, *Org. Lett.* **2009**, *11*, 1607; g) T. S. Mei, X. S. Wang, J. Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 10806; h) M. Wasa, J. Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 14058; i) J. A. Jordan-Hore, C. C. C. Johansson, M. Gulias, E. M. Beck, M. J. Gaunt, *J. Am. Chem. Soc.* **2008**, *130*, 16184; j) W. C. P. Tsang, R. H. Munday, G. Brasche, N. Zheng, S. L. Buchwald, *J. Org. Chem.* **2008**, *73*, 7603; k) G. Brasche, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 1958; *Angew. Chem. Int. Ed.* **2008**, *47*, 1932; l) X. Chen, X. S. Hao, C. E. Goodhue, J. Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790; m) W. C. P. Tsang, N. Zheng, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 14560; n) Q. Wang, S. L. Schreiber, *Org. Lett.* **2009**, *11*, 5178; o) M. Kienle, C. Dunst, P. Knochel, *Org. Lett.* **2009**, *11*, 5158; p) T. Kawano, K. Hirano, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2010**, *132*, 6900; q) H. Q. Zhao, M. Wang, W. P. Su, M. C. Hong, *Adv. Synth. Catal.* **2010**, *352*, 1301; r) H. G. Wang, Y. Wang, C. L. Peng, J. C. Zhang, Q. A. Zhu, *J. Am. Chem. Soc.* **2010**, *132*, 13217; s) S. H. Cho, J. Y. Kim, S. Y. Lee, S. Chang, *Angew. Chem.* **2009**, *121*, 9291; *Angew. Chem. Int. Ed.* **2009**, *48*, 9127; t) M. Miyasaka, K. Hirano, T. Satoh, R. Kowalczyk, C. Bolm, M. Miura, *Org. Lett.* **2011**, *13*, 359; u) S. Guo, B. Qian, Y. Xie, C. Xia, H. Huang, *Org. Lett.* **2011**, *13*, 522.
- [4] For selected examples of C–H amination of activated C_{sp}³–H bonds which include allylic, benzylic C–H bonds, and C–H bonds having heteroatoms or electron-withdrawing substituents on the carbon atom, see: a) M. M. Diaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko, P. J. Perez, *J. Am. Chem. Soc.* **2003**, *125*, 12078; b) M. R. Frutos, S. Trofimenko, M. M. Diaz-Requejo, P. J. Perez, *J. Am. Chem. Soc.* **2006**, *128*, 11784; c) R. Bhuyan, K. M. Nicholas, *Org. Lett.* **2007**, *9*, 3957; d) G. Pelletier, D. A. Powell, *Org. Lett.* **2006**, *8*, 6031; e) J. L. Liang, S. X. Yuan, J. S. Huang, W. Y. Yu, C. M. Che, *Angew. Chem.* **2002**, *114*, 3615; *Angew. Chem. Int. Ed.* **2002**, *41*, 3465; f) J. L. Liang, S. X. Yuan, J. S. Huang, C. M. Che, *J. Org. Chem.* **2004**, *69*, 3610; g) C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc.* **2004**, *126*, 15378; h) K. W. Fiori, J. Du Bois, *J. Am. Chem. Soc.* **2007**, *129*, 562; i) Y. Zhang, H. Fu, Y. Jiang, Y. Zhao, *Org. Lett.* **2007**, *9*, 3813; j) E. Milczek, N. Boudet, S. Blakey, *Angew. Chem.* **2008**, *120*, 6931; *Angew. Chem. Int. Ed.* **2008**, *47*, 6825; k) K. J. Fraunhoffer, M. C. White, *J. Am. Chem. Soc.* **2007**, *129*, 7274; l) S. A. Reed, M. C. White, *J. Am. Chem. Soc.* **2008**, *130*, 3316; m) G. S. Liu, G. Y. Yin, L. Wu, *Angew. Chem.* **2008**, *120*, 4811; *Angew. Chem. Int. Ed.* **2008**, *47*, 4733.

- [5] For an elegant example of intramolecular C–H amination of unactivated C_{sp}³–H bonds, see: J. J. Neumann, S. Rakshit, T. Droge, F. Glorius, *Angew. Chem.* **2009**, *121*, 7024; *Angew. Chem. Int. Ed.* **2009**, *48*, 6892.
- [6] a) H. Y. Thu, W. Y. Yu, C. M. Che, *J. Am. Chem. Soc.* **2006**, *128*, 9048; b) Z. G. Li, D. A. Capretto, R. Rahaman, C. A. He, *Angew. Chem.* **2007**, *119*, 5276; *Angew. Chem. Int. Ed.* **2007**, *46*, 5184; c) C. G. Liang, F. Robert-Pedlard, C. Fruit, P. Muller, R. H. Dodd, P. Dauban, *Angew. Chem.* **2006**, *118*, 4757; *Angew. Chem. Int. Ed.* **2006**, *45*, 4641; d) C. G. Liang, F. Collet, F. Robert-Peillard, P. Muller, R. H. Dodd, P. Dauban, *J. Am. Chem. Soc.* **2008**, *130*, 343; e) B. P. Gomez-Emeterio, J. Urbano, M. M. Diaz-Requejo, P. J. Perez, *Organometallics* **2008**, *27*, 4126; f) F. Collet, C. Lescot, C. G. Liang, P. Dauban, *Dalton Trans.* **2010**, *39*, 10401.
- [7] T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685.
- [8] For reviews on biarylphosphane ligands, see: a) D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 6438; *Angew. Chem. Int. Ed.* **2008**, *47*, 6338; b) D. S. Surry, S. L. Buchwald, *Chem. Sci.* **2011**, *2*, 27.
- [9] For recent reviews on N-heterocyclic carbenes, see: a) S. P. Nolan, *Acc. Chem. Res.* **2011**, *44*, 91; b) H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841; c) N. Marion, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 1440; d) N. Marion, S. Diez-Gonzalez, I. P. Nolan, *Angew. Chem.* **2007**, *119*, 3046; *Angew. Chem. Int. Ed.* **2007**, *46*, 2988.
- [10] N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006**, *128*, 4101.
- [11] a) O. Baudoin, A. Herrbach, F. Gueritte, *Angew. Chem.* **2003**, *115*, 5914; *Angew. Chem. Int. Ed.* **2003**, *42*, 5736; b) J. Hitce, P. Retailleau, O. Baudoin, *Chem. Eur. J.* **2007**, *13*, 792; c) R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654.
- [12] For a related study on benzocyclobutene formation (mechanism and scope), see: M. Chaumontet, R. Piccardi, N. Audic, J. Hitce, J. L. Peglion, E. Clot, O. Baudoin, *J. Am. Chem. Soc.* **2008**, *130*, 15157.
- [13] See the Supporting Information for details.
- [14] a) M. Brookhart, M. L. H. Green, G. Parkin, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6908; b) M. Lafrance, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 14570; c) S. Rousseaux, M. Davi, J. Sofack-Kreutzer, C. Pierre, C. E. Kefalidis, E. Clot, K. Fagnou, O. Baudoin, *J. Am. Chem. Soc.* **2010**, *132*, 10706.
- [15] a) L. J. L. Haller, M. J. Page, S. A. Macgregor, M. F. Mahon, M. K. Whittlesey, *J. Am. Chem. Soc.* **2009**, *131*, 4604; b) C. E. Kefalidis, O. Baudoin, E. Clot, *Dalton Trans.* **2010**, *39*, 10528.