2-Phosphinoimidazole Ligands: N–H NHC or P–N Coordination Complexes in Palladium-Catalyzed Suzuki-Miyaura Reactions of Aryl Chlorides

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ABSTRACT: We report the synthesis of two palladium 2-(dialkylphosphino)imidazole complexes and demonstrate their activity as catalysts for Suzuki-Miyaura reactions with (hetero)aryl chlorides at room temperature. Our mechanistic studies demonstrate that these palladium complexes exist as an equilibrium mixture between the P–N coordinated and N–H NHC forms of ligand. Our studies suggest that the N–H NHC form may be important for high catalytic activity in Suzuki-Miyaura reactions with aryl chlorides. These reactions proceed at or near room temperature in good to excellent yields. Heteroaryl chlorides are also reactive at lower catalyst loadings.

The Suzuki-Miyaura cross-coupling reaction is arguably one of the most versatile reactions for creating Csp^2–Csp^2 bonds. Since its discovery 40 years ago,[1] palladium-catalyzed Suzuki-Miyaura reactions have been used in the synthesis of herbicides, pharmaceuticals, fine chemicals, and natural products.[2] One reason this reaction is favored over other C–C coupling methods is due to its wide utility; mild reaction conditions, combined with a vast number of commercially available boronic acids, makes the Suzuki-Miyaura reaction more practical than other couplings with stoichiometric organometallic reagents. Aryl bromides and iodides are typically employed as cross-coupling partners and can give high yields in short reaction times. Aryl chlorides, however, are much more challenging substrates and the development of new catalysts to address this issue is an ongoing focus in catalysis research. Aryl chlorides are more shelf-stable, more readily available than the corresponding bromides and iodides, and much less expensive.[3] However, this increased stability also makes them harder to activate in the Suzuki-Miyaura reaction, leading to higher temperatures and catalyst loadings.[4, 2b]

Recently, we reported the synthesis of monosubstituted N–H *N*-heterocyclic carbene (NHC) complexes of palladium and demonstrated their high activity in Suzuki-Miyaura reactions with aryl bromides.[5] N–H NHC complexes and the corresponding imidazolyl-type ligands are known to enable efficient catalysis in cross-coupling and other classes of reactions by serving as bifunctional catalysts.[6] We demonstrated that the N–H NHC catalyst (**2a**) could be accessed via non-oxidative P–aryl insertion by palladium into the C–P bond of a 2-(diarylphosphino)imidazole ligand such as **1a** (Figure 1).[7] Under our standard reaction conditions, the N–H of complex **2a** is deprotonated to form an X-type imidazolyl ligand.[6a] Tolman electronic parameter comparisons between this ligand and other common NHC ligands showed that the anionic imidazolyl ligand of **2a** was significantly more donating in Suzuki-Miyaura cross-couplings. The ν_{CO} value was shifted by >40 cm^{-1} for DFT-calculated $Ni(CO)_3(NHC)$ structures.[5] Unfortunately, diarylphosphine complexes like **2a** had very low reactivity towards cross-couplings with aryl chloride substrates. Beller has previously reported that 2-(dialkylphosphino)imidazole ligands (**3** or **4**) enable highly efficient Pd-catalyzed Suzuki-Miyaura reactions and Buchwald-Hartwig aminations with aryl chloride substrates.[8] Based on this precedence and our recent findings, we wondered whether P-alkyl-substituted phosphinoimidazole ligands also undergo P–imidazole bond insertion to form N–H NHC complexes with palladium and if these N–H NHC species were responsible for the high activity of the catalysts as observed by Beller and other researchers.[9] In this report, we synthesize two new P-alkyl 2-phosphinoimidazole palladium complexes and demonstrate that an equilibrium exists between the P–N phosphinoimidazole complex and the corresponding N–H NHC complex.[10] These studies suggest that the N–H NHC palladium complex may play an important role in catalysis when 2-phosphinoimidazole ligands are employed in palladium-catalyzed reactions.

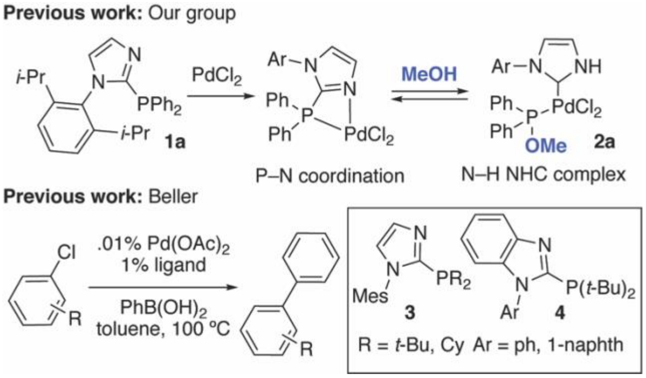


Figure 1. 2-Phosphinoimidazole-based palladium catalysis.

To begin, we synthesized the corresponding di-tert-butyl (**1b**) and dicyclohexyl (**1c**) phosphinoimidazole ligand derivatives of **1a**, which have previously been reported by Beller (Figure 2a).[9e] As observed previously, when ligand **1a** is mixed with $PdCl_2$ in methanol, complex **2a** is isolated as the only product and complex **5a** is not observed. In contrast, when ligand **1b** containing P-*t*Bu substituents was used, complex **5b** was isolated in 96% yield as the only product of the reaction. X-ray quality single crystals of **5b** were grown and the X-ray structure was obtained to confirm its structure as a P–N palladium complex (Figure 2b). Complex **5b** was previously reported.[9f] When dicyclohexyl derivative **1c** was reacted, a ~4:1 mixture of products **2c** and **5c** were observed by NMR (69% yield).

When the mixture was subjected to crystallization conditions, an X-ray quality crystal of **2c** was obtained (Figure 2b). The X-ray structure of **2c** confirms the potential of the P-alkyl phosphinoimidazole ligands to form N–H NHC complexes with palladium and suggests that these types of N–H NHC ligands may help facilitate Suzuki reactions in catalysis. [7b]

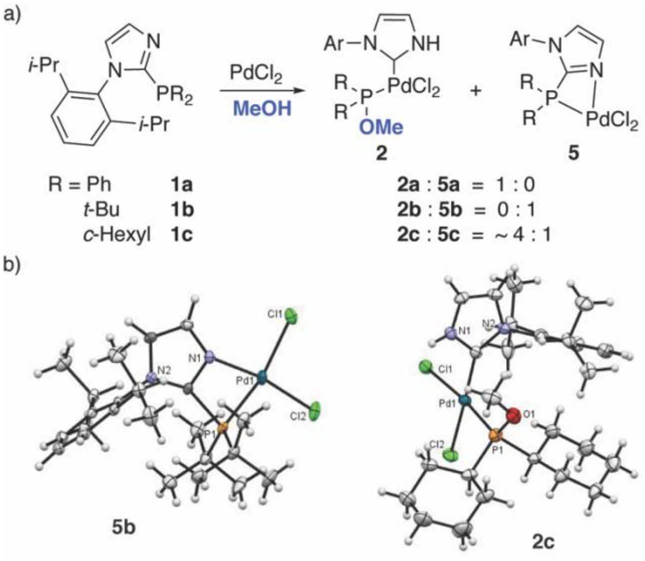
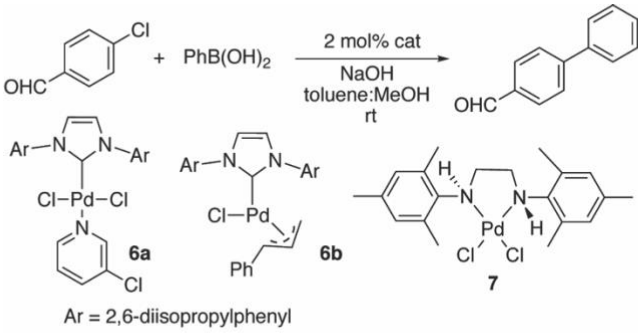


Figure 2. a) Synthesis of Pd-phosphinoimidazole complexes. b) X-ray crystal structures of **5b** and **2c**.

We next sought to investigate the catalytic efficiency of these new palladium complexes in the Suzuki-Miyaura reaction with less reactive aryl chloride substrates. We chose 4-chlorobenzaldehyde for our optimization studies because it is known to be a difficult substrate; the aldehyde is unstable at high temperature, which leads to poor yields and conversions under standard Suzuki conditions.[11] We found that at ambient temperature, diphenylphosphino catalyst **2a** provided only 5% conversion to product (Table 1, entry 1). This result is consistent with what we had observed previously with aryl chloride substrates. However, when complex **5b** or the mixture of **2c** and **5c** were employed (entries 2–3), both reactions proceeded to 100% conversion in less than 4 h (79% isolated yield for catalyst **5b**, R = t-butyl). Importantly, we saw only a small difference in reactivity between the t-butyl (**5b**) and cyclohexyl (**2c** + **5c**) substituted catalysts. This was intriguing to us because the ratio of the N–H NHC and P–N complexes (**2** and **5**) are dramatically different for the two ligands. When pure N–H NHC complex **2c** was employed (after purification by crystallization), the reaction conversion remained high (entry 4). Additionally, we observed that methanol was essential as a co-solvent to achieve high rates of catalysis with both t-butyl and cyclohexyl complexes. The Absence of methanol in the reactions leads to no product formation with **5b** (entry 5) and 39% conversion with the mixture of **2c** + **5c** (entry 6). Previously we have found that methanol is essential for formation of the N–H NHC complex to occur,[5] which suggests that the N–H NHC form of the t-butyl catalyst (**2b**) may actually be present in the reaction. The fact that the mixture of **2c** + **5c** does give some product in the absence of methanol further supports our hypothesis that the N–H NHC form of the catalyst is important for efficient catalysis. When we performed the Suzuki reaction with 20 mol% catalyst **5b**, we observed in the ^{31}P NMR clear signs of formation of the N–H NHC complex **2b** (characteristic Pd-PR_2OMe peaks in the ^{31}P NMR) and mass spectrometry confirmed the presence of complex **2b** in the reaction (see Supporting Information (SI)). These results suggest that the N–H NHC form of these palladium complexes may in fact be the active species in catalysis that enables high reactivity in the Suzuki-Miyaura reaction with aryl chlorides.

Table 1. Optimization of Suzuki-Miyaura reaction with aryl chlorides.



entry[a]	catalyst	% Conv.[b]
1	**2a**	5
2	**5b**	100 (79)
3	**2c+5c**	100 (76)
4	**2c**	94 (70)
5[c]	**5b**	0
6[c]	**2c+5c**	39
7	**6a**	100
8	**6b**	100
9	**7**	8
10	$PdCl_2$	6
11	**1b**	0
12[d]	**5b**	28
13[e]	**5b**	34
14[f]	**5b**	100
15[g]	**5b**	100
16[h]	**5b**	13

[a] Reaction run with catalyst (0.02 mmol, 2%), 4-chlorobenzaldehyde (1.0 mmol, 1 eq), phenylboronic acid (1.5 mmol, 1.5 eq), and sodium hydroxide (2.0 mmol, 2 eq) at room temperature for 4 hours in 3.3 mL toluene with 5% methanol. [b] Percent conversion determined by ^{1}H NMR by comparing product formed to remaining starting material aryl chloride. Numbers in parenthesis indicate isolated yield. [c] Run in 100% toluene. [d] With Cs_2CO_3 (2 equiv). [e] With NaOtBu (2 equiv). [f] Run in 100% EtOH with K_2CO_3 as base. [g] Run with 1 mol% **2b** for 14 h. [h] Run with 0.1 mol% **2b** for 24 h.

Our optimization studies showed that the resulting catalytic activity of our new phosphinoimidazole palladium complexes in Suzuki reactions with aryl chlorides was comparable to those reported previously.[8] Although the catalyst loading is higher with our catalyst, the reaction can be run at lower temperatures, which can provide important advantages with sensitive substrates. Thus, we performed additional studies to further optimize the reactivity of our catalyst. We found that when compared to state-of-the-art PEPPSI (**6a**),[11] cinnamyl-NHC

(**6b**),[12] and diamine (**7**)[13] palladium catalysts, our phosphinoimidazole catalysts performed as well or better under our standard conditions (Table 1, entries 7-9). We found that the phosphinoimidazole ligand is essential for catalysis to occur (entry 10) and that palladium is necessary for product formation (entry 11). We also screened other bases (entries 12-13) and found that sodium hydroxide was the best base for the reaction under these conditions. The reaction can also proceed in ethanol with K_2CO_3 as the base with excellent reactivity (entry 14).[12b,14] Finally, we tested how much we can lower the catalyst loading and still maintain high yield of product when the reaction is run at room temperature. At 1 mol% **5b**, the reaction reached completion in 14 h (entry 15). Unfortunately, lower concentrations resulted in minimal reactivity (entry 16).

With our optimized conditions in hand, we next wanted to confirm that catalyst **5b** maintained high reactivity across a variety of (hetero)aryl chloride substrates (Figure 3). Many of the substrates tested required elevated temperatures (40-80 °C) in order to provide high yields (see SI for details). Good functional group tolerance was seen with aryl chlorides containing both electron-donating and withdrawing functional groups (**9a** – **9n**). Notably, 4-chlorophenol (**9b**) is a particularly challenging substrate for Suzuki cross-couplings because it is deprotonated under the reaction conditions, and we only achieved small conversion to product. More sterically hindered substrates (**9k–9n)** also underwent the Suzuki-Miyaura reaction readily. Heteroaryl chlorides, which are notoriously difficult substrates for Suzuki reactions, also proceeded in good yields under increased reaction times (**9o**–**9v**). Due to the difficult nature of activating heteroaryl chlorides, these reactions required higher temperatures, but could be run with 1% of catalyst. We were particularly happy to find that various *N*-heterocycles also gave moderate to good yields with our catalyst (**9q** – **9v**).

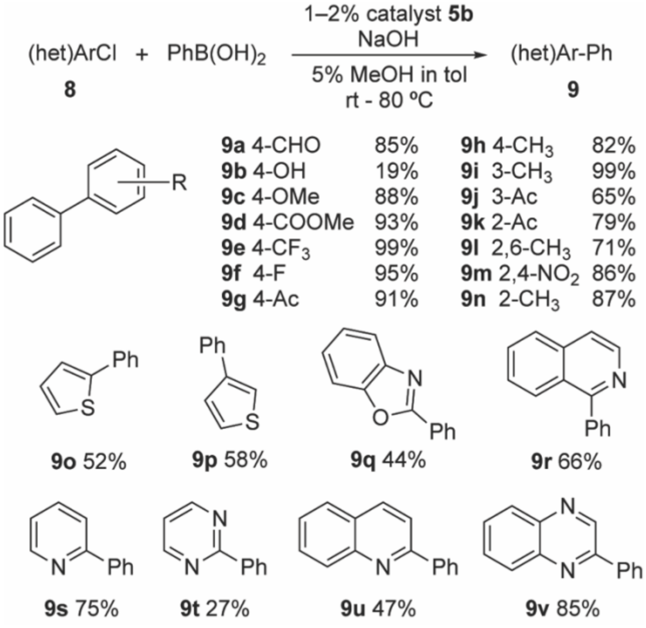


Figure 3. Substrate scope for Suzuki-Miyaura reaction.

In conclusion, we have synthesized and characterized two new palladium catalysts with 2-(dialkylphosphino)imidazole ligands. Our studies demonstrate the presence of an equilibrium between the palladium P–N phosphinoimidazole species and the corresponding N–H NHC complex in the presence of methanol and during catalysis. Our studies suggest that the N–H NHC form of the phosphinoimidazole catalyst may be important for high catalytic activity in catalysis with these ligands. These catalysts were optimized for the Suzuki-Miyaura reaction and were shown to perform with higher reactivity that P-aryl substituted 2-phosphinoimidazole ligands in cross-coupling reactions with aryl chloride substrates at or near room temperature. Heteroaryl chlorides are also reactive at lower catalyst loadings to give moderate to good yields. Future work in our lab will include further mechanistic and computational studies to investigate the role of the N–H NHC (**2b**) vs P–N (**5b**) palladium complexes during catalysis, as well as applying 2-(dialkylphosphino)imidazole ligands to other transition metal catalyzed reactions.

ASSOCIATED CONTENT

Supporting Information.

Full procedures for the synthesis of ligands, Pd-NHC and Pd-P–N complexes, and for conducting catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) (a) Suzuki, A. Recent Advances in the Cross-Coupling Reactions of Organoboron Derivatives with Organic Electrophiles, 1995–1998. *J. Organomet. Chem.* **1999**, *576,* 147–168. (b) Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95,* 7, 2457–2483. (c) Miyaura, N.; Yamada, K.; Suzuki, A. A New Stereospecific Cross-Coupling by the Palladium-Catalyzed Reaction of 1-Alkenylboranes with 1-Alkenyl or 1-Alkynyl Halides. *Tetrahedron Lett.* **1979**, *20,* 36, 3437–3440.

(2) (a) Buskes, M. J.; Blanco, M.-J. Impact of Cross-Coupling Reactions in Drug Discovery and Development. *Molecules* **2020**, *25,* 15, 3493. (b) Bhaskaran, S.; Padusha, M. S.; Sajith, A. M. Application of Palladium Based Precatalytic Systems in the Suzuki-Miyaura Cross-Coupling Reactions of Chloro- Heterocycles. *ChemistrySelect* **2020**, *5,* 9005–9016. (c) Devendar, P.; Qu, R.-Y.; Kang, W.-M.; He, B.; Yang, G.-F. Palladium-Catalyzed Cross-Coupling Reactions: A Powerful Tool for the Synthesis of Agrochemicals. *J. Agric. Food Chem.* **2018**, *66,* 34, 8914–8934. (d) Torborg, C.; Beller, M. Recent Applications of Palladium-Catalyzed Coupling Reactions in the Pharmaceutical, Agrochemical, and Fine Chemical Industries. *Adv. Synth. Catal.* **2009**, *351,* 3027–3043.

(3) (a) Schlummer, B.; Scholz, U. Palladium-Catalyzed C–N and C–O Coupling–A Practical Guide from an Industrial Vantage Point. *Adv. Synth. Catal.* **2004**, *346,* 1599–1626. (b) Littke, A. F.; Fu, G. C. Palladium-Catalyzed Coupling Reactions of Aryl Chlorides. *Angew. Chem. Int. Ed.* **2002**, *41,* 4176–4211.

(4) (a) Ouyang, J.-S.; Li, Y.-F.; Huang, F.-D.; Lu, D.-D.; Liu, F.-S. The Highly Efficient Suzuki–Miyaura Cross-Coupling of (Hetero)aryl

Chlorides and (Hetero)arylboronic Acids Catalyzed by “Bulky-yet-Flexible” Palladium–PEPPSI Complexes in Air. *ChemCatChem* **2018**, *10,* 371–375. (b) Xu, L.-Y.; Liu, C.-Y.; Liu, S.-Y.; Ren, Z.-G.; Young, D. J.; Lang, J.-P. Suzuki-Miyaura Cross-Coupling Reaction of Aryl Chlorides with Aryl Boronic Acids Catalyzed by a Palladium Dichloride Adduct of N-Diphenylphosphanyl-2-aminopyridine. *Tetrahedron* **2017**, *73,* 3125–3132. (c) Dasa, P.; Linert, W. Schiff Base-Derived Homogeneous and Heterogeneous Palladium Catalysts for the Suzuki–Miyaura Reaction. *Coord. Chem. Rev.* **2016**, *311,* 1–23.

(5) Martinez, E. E.; Jensen, C. A.; Larson, A. J. S.; Kenney, K. C.; Clark, K. J.; Nazari, S. H.; Valdivia-Berroeta, G. A.; Smith, S. J.; Ess, D. H.; Michaelis, D. J. Monosubstituted, Anionic Imidazolyl Ligands from N−H NHC Precursors and Their Activity in Pd-Catalyzed Cross-Coupling Reactions. *Adv. Synth. Catal.* **2020**, *362,* 14, 2876–2881.

(6) (a) Zhu, J.; Lindsay, V. N. G. Benzimidazolyl Palladium Complexes as Highly Active and General Bifunctional Catalysts in Sustainable Cross-Coupling Reactions. *ACS Catal.* **2019**, *9,* 8, 6993–6998. (b) Kuwata, S.; Hahn, F. E. Complexes Bearing Protic N-Heterocyclic Carbene Ligands. *Chem. Rev.* **2018**, *118,* 9642–9677. (c) Jahnke, M. C.; Hahn, F. E. Complexes with Protic (NH,NH and NH,NR) N-heterocyclic Carbene Ligands. *Coord. Chem. Rev.* **2015**, *293–294,* 95–115. (d) Kuwata, S.; Ikariya, T. Metal–Ligand Bifunctional Reactivity and Catalysis of Protic N-Heterocyclic Carbene and Pyrazole Complexes Featuring β-NH Units. *Chem. Commun.* **2014**, *50,* 14290–1430. (e) Hahn, F. E. Substrate Recognition and Regioselective Catalysis with Complexes Bearing NR,NH–NHC Ligands. *ChemCatChem* **2013**, *5,* 419–430. (f) Kuwata, S.; Ikariya, T. β-Protic Pyrazole and N-Heterocyclic Carbene Complexes: Synthesis, Properties, and Metal–Ligand Cooperative Bifunctional Catalysis. *Chem. Eur. J.* **2011**, *17,* 3542–3556.

(7) (a) Chang, Y.-C.; Chang, C.-H.; Wang, L.-W.; Liang, Y.-H.; Hu, D.-F.; Weng, C.-M.; Mao, K.-C.; Hong, F.-E. Imidazolio-Substituted Secondary Phosphine Oxides as Potential Carbene Reagents. *Polyhedron* **2015**, *100,* 382–391. (b) Abdellah, I.; Lepetit, C.; Canac, Y.; Duhayon, C.; Chauvin, R. Imidazoliophosphines are True N-Heterocyclic Carbene (NHC)–Phosphenium Adducts. *Chem. Eur. J.* **2010**, *16,* 13095–13108.

(8) (a) Zapf, A.; Beller, M. The Development of Efficient Catalysts for Palladium-Catalyzed Coupling Reactions of Aryl Halides. *Chem. Commun.* **2005**, 431–440. (b) Harkal, S.; Rataboul, F.; Zapf, A.; Fuhrmann, C.; Riermeier, T.; Monsees, A.; Beller, M. Dialkylphosphinoimidazoles as New Ligands for Palladium-Catalyzed Coupling Reactions of Aryl Chlorides. *Adv. Synth. Catal.* **2004**, *346,* 1742–1748.

(9) (a) Fleischer, I.; Wu, L.; Profir, I.; Jackstell, R.; Franke, R.; Beller, M. Towards the Development of a Selective Ruthenium-Catalyzed Hydroformylation of Olefins. *Chem. Eur. J.* **2013**, *19,* 10589–10594. (b) Wu, L.; Fleischer, I.; Jackstell, R.; Profir, I.; Franke, R.; Beller, M. Ruthenium-Catalyzed Hydroformylation/Reduction of Olefins to Alcohols: Extending the Scope to Internal Alkenes. *J. Am. Chem. Soc.* **2013**, *135,* 14306–14312. (c) Grotjahn, D. B.; Incarvito, C. D.; Rheingold, C. L. Combined Effects of Metal and Ligand Capable of Accepting a Proton or Hydrogen Bond Catalyze Anti-Markovnikov Hydration of Terminal Alkynes. *Angew. Chemie. Int. Ed.* **2001**, *40,* 20, 3884–3887. (d) Schmid, T. E.; Jones, D. C.; Songis, O.; Diebolt, O.; Furst, M. R. L.; Slawin, A. M. Z.; Cazin, C. S. J. Mixed Phosphine/N-Heterocyclic Carbene Palladium Complexes: Synthesis, Characterization and Catalytic use in Aqueous Suzuki–Miyaura Reactions. *Dalton Trans.* **2013**, *42,* 7345–7353. (e) Schulz, T.; Torborg, T.; Schäffner, B.; Huang, J.; Zapf, A.; Kadyrov, R.; Börner, A.; Beller, M. Practical Imidazole-Based Phosphine Ligands for Selective Palladium-Catalyzed Hydroxylation of Aryl Halides. *Angew. Chem. Int. Ed.* **2009**, *48,* 918–921. f) Torborg, C.; Huang, J.; Schulz, T.; Schäffner, B.; Zapf, A.; Spannenberg, A.; Börner, A.; Beller, M. Improved Palladium-Catalyzed Sonogashira Coupling Reactions of Aryl Chlorides. *Chem.-Eur. J.* **2009**, *15,* 1329–1336.

(10) (a) Wong, S. M.; So, C. M.; Kwong, F. Y. The Recent Development of Phosphine Ligands Derived from 2-Phosphino-substituted Heterocycles and their Applications in Palladium-Catalyzed Cross-Coupling Reactions. *Synlett* **2012**, *23,* 1132–1153. (b) Grotjahn, D. B. Bifunctional Catalysts and Related Complexes: Structures and Properties. *Dalton Trans.* **2008**, 6497–6508. (c) Diez, V.; Espino, G.; Jalon, F. A.; Manzano, B. R.; Perez-Manrique, M. Synthesis and Structure of New Palladium Complexes with the Ligand 2-(Diphenylphosphino)-1-methylimidazole: Evidence of Hemilability. *J. Organomet. Chem.* **2007**, *692,* 7, 1482–1495.

(11) (a) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. C. Easily Prepared Air- and Moisture-Stable Pd–NHC (NHC=N-Heterocyclic Carbene) Complexes: A Reliable, User-Friendly, Highly Active Palladium Precatalyst for the Suzuki–Miyaura Reaction. *Chem. Eur. J.* **2006**, *12,* 4743–4748. (b) Diebolt, O.; Jurčík, V.; Correa da Costa, R.; Braunstein, P.; Cavallo, L.; Nolan, S. P.; Slawin, A. M. Z.; Cazin, C. S. J. Mixed Phosphite/N-Heterocyclic Carbene Complexes: Synthesis, Characterization and Catalytic Studies. *Organometallics* **2010**, *29,* 1443–1450. (c) Zinser, C. M.; Warren, K. G.; Meadows, R. E.; Nahra, F.; Al-Majid, A. M; Barakat, A.; Islam, M. S.; Nolan, S. P.; Cazin, C. S. J. Towards Environmentally Friendlier Suzuki–Miyaura Reactions with Precursors of Pd-NHC (NHC = N-Heterocyclic Carbene) Complexes. *Green Chem.* **2018**, *20,* 3246–3252. (d) Nahra, F.; Cazin, C. S. J. Sustainability in Ru- and Pd-based Catalytic Systems Using N-Heterocyclic Carbenes as Ligands. *Chem. Soc. Rev.* **2021**, *50,* 3094-3142.

(12) (a) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. Modified (NHC)Pd(allyl)Cl (NHC = N-Heterocyclic Carbene) Complexes for Room-Temperature Suzuki−Miyaura and Buchwald−Hartwig Reactions. *J. Am. Chem. Soc.* **2006**, *128,* 12, 4101–4111. (b) Izquierdo, F.; Corpet, M.; Nolan, S. P. The Suzuki–Miyaura Reaction Performed Using a Palladium–N-Heterocyclic Carbene Catalyst and a Weak Inorganic Base. *Eur. J. Org. Chem.* **2015**, 1920–1924.

(13) Liu, G.; Han, F.; Liu, C.; Wu, H.; Zeng, Y.; Zhu, R.; Yu, X.; Rao, S.; Huang, S.; Wang, J. A Highly Active Catalyst System for Suzuki–Miyaura Coupling of Aryl Chlorides. *Organometallics* **2019**, *38,* 7, 1459–1467.

(14) (a) Huo, P.; Li, J.; Liu, W.; Mei, G. Highly Efficient Bulky α-Diimine Palladium Complexes for Suzuki-Miyaura Cross-Coupling Reaction. *Chin. J. Chem.* **2017**, *35,* 363–367. (b) Qiu, J.; Wang, L.; Liu, M.; Shen, Q.; Tang, J. An efficient and simple protocol for a $PdCl_2$-ligandless and additive-free Suzuki coupling reaction of aryl bromides. *Tetrahedron Lett.* **2011**, *52,* 6489–6491.

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