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Review

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Exploring sterically-demanding triarylphosphine ligands to enhance activation of challenging C-Cl bonds in palladium catalysis

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This paper is dedicated to the memory of Professor Amitabha Sarkar

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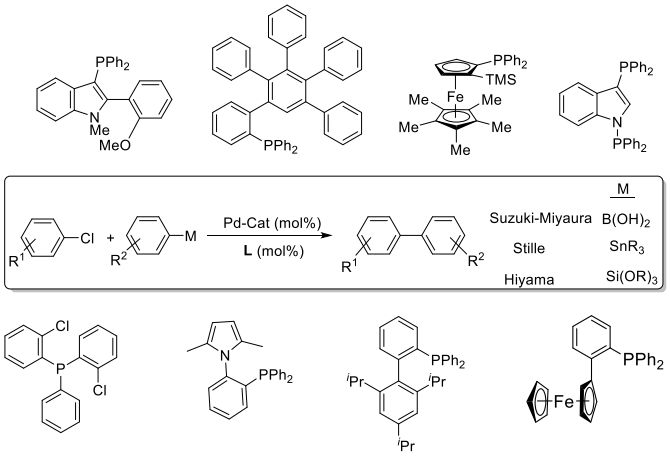
Abstract

The effectiveness of palladium-catalyzed coupling reactions is greatly influenced by the ligand environment surrounding the palladium catalysts. Many researchers have focused on developing new ligands to enhance the reactivity of chloroarenes, which are plentiful but often unreactive. Recent progress has introduced various ligands designed to address these issues. Despite these advancements, establishing clear links between ligand structure and reactivity remains difficult, though alkylphosphines generally show better performance than arylphosphines and N-heterocyclic carbenes facilitate reactions carried out under milder conditions. This mini-review emphasizes recent advancements in ligand synthesis aimed at activating aryl chlorides in coupling reactions catalyzed by palladium. We divide our discussion into three main categories: sterically demanding, electron-rich alkylphosphine ligand-containing palladium catalysts; bulky N-heterocyclic carbene-containing palladium catalysts and sterically demanding triarylphosphine ligand-containing palladium catalysts. The review also focuses on various catalytic activation mechanisms that aid in forming challenging carbon-carbon and carbon-heteroatom bonds and includes a brief overview of substrate scope, limitations and reaction mechanisms involved in these transformations.



Keywords: Triarylphosphine, catalysis, palladium, chloroarenes, cross-coupling, ligand design

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1. Introduction

Carbon-carbon bonds truly form the backbone of organic chemistry, serving as the foundation for the diverse molecules that constitute life[1-4]. The significance of carbon-carbon bonds in chemistry is highlighted by the five Nobel Prizes awarded for key reactions that form them: Wittig reaction, Alkene metathesis, Grignard reaction, Diels-Alder reaction and Cross-coupling reactions. Palladium-catalyzed cross-coupling reactions are particularly valuable due to their ability to form carbon-heteroatom and carbon-carbon bonds under mild conditions, maintaining the integrity of various functional groups with exceptional selectivity. This versatility makes these reactions essential for synthesizing highly complex molecules[5-7] Many monographs and reviews highlight the increasing popularity of palladium-catalyzed cross-coupling reactions in a range of areas, from synthetic organic chemistry to materials science[8-16]. Figure 1 outlines the different types of C-C cross-coupling reactions.

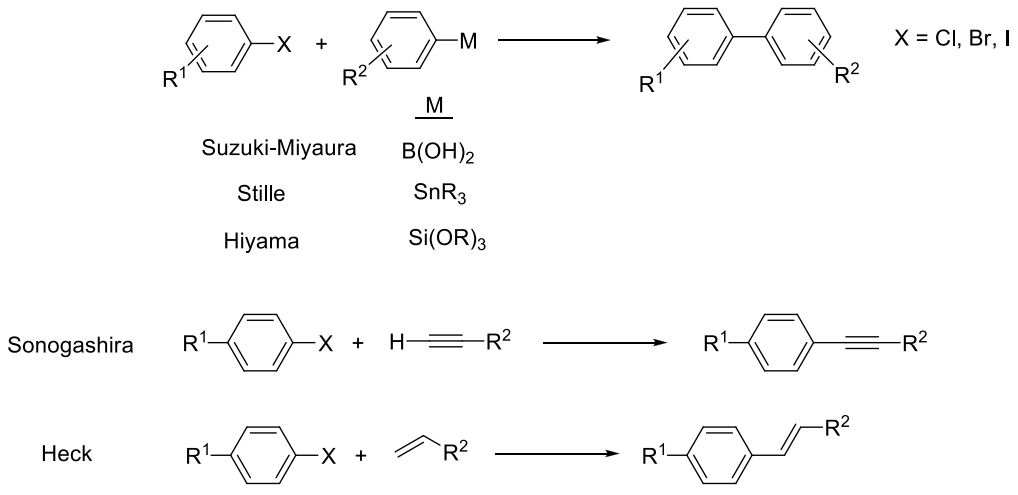


Figure 1. Various types of C-C cross-coupling reactions.

In synthetic laboratories, common catalyst systems include widely used complexes like $[Pd(PPh_3)_4]$ or similar catalysts formed in situ from a triarylphosphine and an appropriate Pd(0) or Pd(II) precursor[17-18]. In these cases, palladium is typically reduced *in situ* to generate an active Pd(0) species. However, these 'classical' catalyst systems have two main drawbacks: they often require high catalyst loading, usually several mol% of Pd and they do not exhibit activity with more demanding aryl chloride substrates. Although chloroarenes are more cost-effective and readily available compared to their bromide and iodide

counterparts, their reduced reactivity is attributed to the stronger C-Cl bond (95 kcal/mol) compared to C-Br (79 kcal/mol) and C-I bonds (64 kcal/mol). This stronger bond hinders the oxidative addition, which is often the rate-determining step in these reactions.

The effectiveness of palladium-catalyzed C-Cl bond activation is highly dependent on the ligand environment around the palladium center[19-21]. Many research groups have focused on developing new ligands to improve the reactivity of chloroarenes. Recent progress has led to the creation of various ligands designed to address these issues. However, determining precise correlations between ligand structure and reactivity remains challenging. Generally, alkylphosphines tend to perform better than arylphosphines, and N-heterocyclic carbenes facilitate reactions under milder conditions.

This review summarizes recent advancements in ligand design specifically aimed at activating aryl chlorides in palladium-catalyzed coupling reactions. We focus less on alkylphosphine and N-heterocyclic carbene ligands due to their high cost. In contrast, aryl phosphines present a promising, cost-effective alternative because, they are more stable and need less precautions against aerial oxidation. Among them, triarylphosphine ligands are particularly attractive if they can achieve catalytic activity comparable to that of aryldialkylphosphine or trialkylphosphine ligands. Various triarylphosphines have been extensively studied for their effectiveness in coupling reactions with chloroarenes. The discussion is divided into three main sections: (a) Mechanistic insights into C-Cl bond activation, (b) A brief review of palladium-catalyzed C-Cl bond activation using bulky, electron-rich alkylphosphine and N-heterocyclic carbene ligands, and (c) Progress in developing palladium catalysts supported by bulky triarylphosphine ligands. Special emphasis is placed on the catalytic activation mechanisms that enable the formation of difficult carbon-carbon and carbon-heteroatom bonds. Additionally, the review includes an analysis of substrate scope, limitations, and the underlying reaction mechanisms driving these transformations.

2. Mechanistic Insights for carbon-chlorine bond activation

Several research groups have attempted the challenge of improving the reactivity of chloroarenes through innovative ligand design[22-24]. To fully appreciate these advancements, it is crucial to first understand the detailed mechanism involved. Figure 2 outlines the four distinct steps in the catalytic cycle.

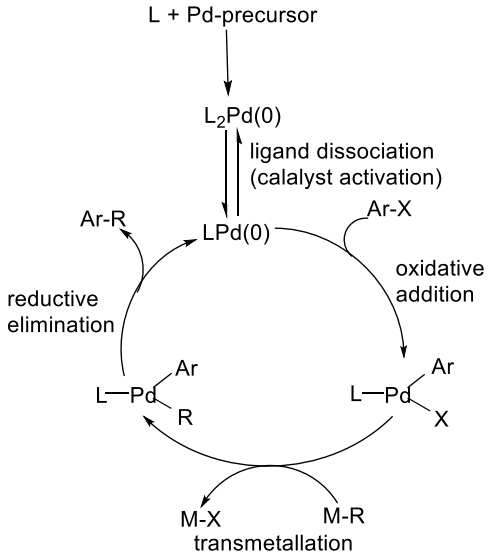


Figure 2. Mechanistic pathways in palladium-catalyzed coupling reactions.

First, we must consider the formation of the catalytically active species from the palladium precursor. Once the 'true' catalyst is formed, the next step is the oxidative addition of the aryl halide to the palladium(0) center. This is followed by a transmetalation reaction, with the final step being the reductive elimination of the product. Since the formation of the catalytically active species and the oxidative addition of palladium(0) to the aryl chloride bond are crucial for determining the overall rate of the coupling reaction, the following discussion will focus on these critical aspects.

The focus initially should be on the formation of catalytically active species from palladium precursors. Research has shown that the choice of palladium source can have a significant impact on the catalytic cycle even when using the same phosphine or carbene ligand. For example, Hartwig and colleagues recently investigated the amination of five-membered heterocyclic halides using palladium as the catalyst[25]. Their study examined various palladium precursors in combination with $^{t}Bu_3P$ as catalysts in the reaction between 3-bromothiophene and N-methylaniline (Figure 3). The observations reported in this paper strongly suggest that the efficiency of the formation of the monophosphine complex [Pd($^{t}Bu_3P$)] controls the rate of the amination reaction.

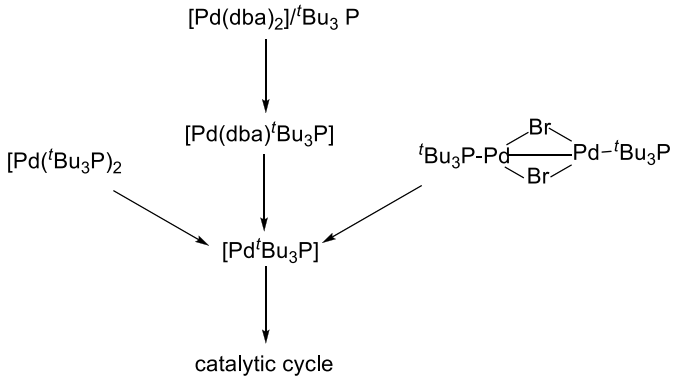


Figure 3. Formation of catalytically active species from palladium precursors.

Similar findings have been documented by Littke and Fu, who employed $^{t}Bu_3P$ in palladium-catalyzed carbon-carbon bond formation[23]; Glorius and colleagues, who used bulky carbenes as supporting ligands[26]; and Buchwald and co-workers, who applied (biphenyl)phosphines in carbon-carbon and carbon-nitrogen bond-forming reactions[27-28]. These studies underscore the importance of forming monoligated [LPd] species for determining the catalytic rate. An equilibrium between [LPd] and [L_2Pd] exists, typically favoring [LPd] when the ligand (L) is large enough to provide significant steric hindrance (see Figure 4).

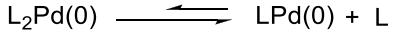
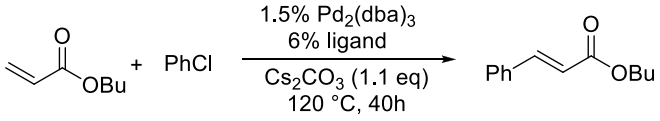


Figure 4. Equilibrium between [LPd] and [L_2Pd] species.

In such cases, the steric bulk of the ligand is essential for protecting and stabilizing the palladium center, thereby preventing catalyst decomposition. Recent reviews have highlighted that the formation of mono-ligated Pd(0)-L species is now recognized as a crucial factor for achieving highly activated catalysis[29-30].Numerous studies have explored how different ligands affect the oxidative addition step in catalytic cycles. Sterically demanding ligands can stabilize palladium complexes with low coordination (LPd), which are more reactive due to their lower electron count. In contrast, electron-donating ligands promote the formation of

more electron-rich metal complexes, accelerating oxidative addition reactions. Brown and colleagues demonstrated that the bulkiness of the ligand significantly impacts the mechanism of aryl chloride addition to zerovalent [PdL_2] complexes (Figure 5)[31]. Their comprehensive study utilized a series of complexes, [$Pd(^tBu_{3-n}Cy_3P)_2$] (where n = 0 – 3), featuring ligands with varying steric bulk.



Ligand	Cy_3P	$^tBuCy_2P$	$^tBu_2CyP$	$^tBu_3P$
yield (%)	0	7	53	58

Figure 5. Impact of ligands on oxidative addition steps.

The findings show that complexes with R_3P = $^tBu_3P$ or $^tBu_2CyP$ exhibit accelerated oxidative addition. This suggests that increasing the bulkiness of the ligand enhances the rate at which Pd(0) undergoes oxidative addition to less reactive Ar-Cl bonds.

Recent work by Hartwig and colleagues supports the dissociative mechanism for sterically demanding phosphines. They isolated a number of tricoordinated palladium(II) compounds with the common formula [$Pd(Ph)X(R_3P)$] (where R_3P = $^tBu_2AdP$, $^tBu_3P$)[32-33]. Their studies showed that the rates of oxidative addition reactions forming [$Pd(Ph)X(R_3P)$] complexes closely match the catalytic rates observed in related cross-coupling reactions. Detailed X-ray crystallography of these complexes showed a T-shaped geometry with the phenyl ring oriented *trans* to the open coordination site on the metal. Structural analysis also identified weak agostic interactions between C-H bond from a ligand and the palladium centre, which were proposed to stabilize the unique geometry of these complexes. These tricoordinated species are particularly notable in palladium-catalyzed coupling reactions, as they illustrate the feasibility of creating monophosphine complexes where both coupling substrates are coordinated to the metal centre.

The significance of reductive elimination and the transmetalation steps is minimized here, as they operate independently of the halide and are not discussed in detail within this context. Based on the mechanistic insights provided, the effective design of ligands for chloroarene activation relies on both electronic and steric factors. Generally, coupling reactions involving chloroarenes are enhanced by using ligands that are both bulky and electron-rich

3. Catalysts Utilizing Bulky, Electron-Rich Alkylphosphines and N-Heterocyclic Carbenes

Several research groups have developed sterically demanding, electron-rich phosphine ligands to improve the activation of chloroarenes. While many alkylphosphine ligands are detailed in the literature, we focus on representative examples categorized into two primary motifs (Figure 6). The first motif comprises highly bulky alkyl phosphines (**A** and **B**)[34-35]. The second motif features a biphenyl backbone with a dialkylphosphino group attached at the 2-position of a phenyl ring. Ligands developed by Buchwald (**C**)[36], Beller (**D** and **E**)[37-38], and Kwong (**F**)[39-40] illustrate this second motif (Figure 6).

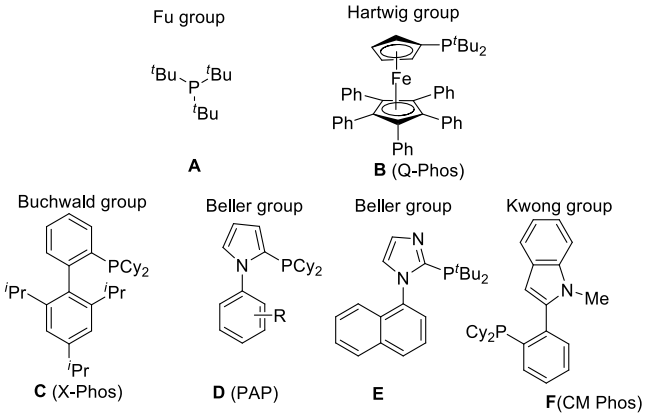


Figure 6. Sterically hindered and electronically rich alkyl phosphine ligands.

These ligands are highly effective due to their electron-rich nature, which increases the electron density on palladium centre and facilitates the oxidative addition step. Additionally, their significant bulkiness encourages the generation of monoligated LPd(0) species, which are essential for the oxidative addition of Pd(0) to unreactive carbon-chlorine bonds. These catalysts proved successful in coupling challenging substrates, including Csp^3-Csp^3 couplings and the synthesis of tetra-substituted biaryls, even at low catalyst loadings.

While phosphine-based ligands have long been studied for enhancing catalytic efficiency in cross-coupling reactions, N-heterocyclic carbene (NHC) ligands gained attention for their beneficial properties, especially due to the excellent thermal stability of the palladium-NHC bond[41-42]. The strong interaction between the electron-rich carbene and the metal center extends catalyst lifetimes and ensures consistent reactivity throughout the reaction. Several monoligated Pd-NHC complexes was synthesized showcasing exceptional reactivity, as demonstrated by the work of Caddick and Cloke[43], Bellemin-Laponnaz and Gade[44], Nolan[45-48], Beller[49], Organ[50] and Herrmann[51] (see Figure 7).

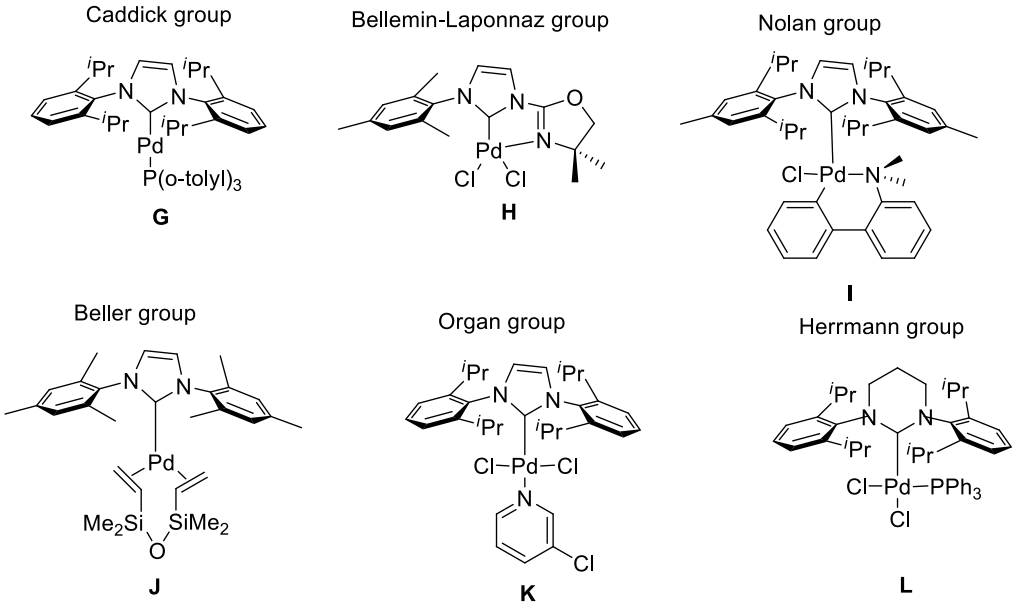


Figure 7. Sterically demanding N-heterocyclic carbenes ligands.

The activity of complexes **G** – **L** was found to correlate with the steric environment around the palladium centre; generally, bulkier NHC ligands lead to increased catalytic activity[52]. Similar to alkylphosphines, the NHC ligands effectively facilitate the activation of C-Cl bonds, often performing efficiently at room temperature and with low catalyst loadings.

Despite the development of several effective NHC carbene and alkylphosphine ligands for chloroarene activation, these systems have notable limitations. Firstly, many of these ligands are susceptible to oxidation and unstable in air, requiring storage under argon. Moreover, these ligands are often quite expensive. The costs of these ligands, as sourced from Strem Chemicals, are detailed below (Figure 8).

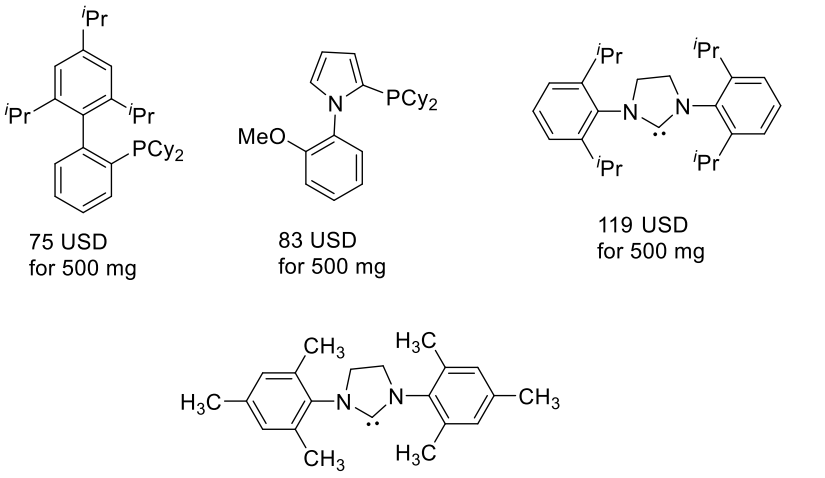
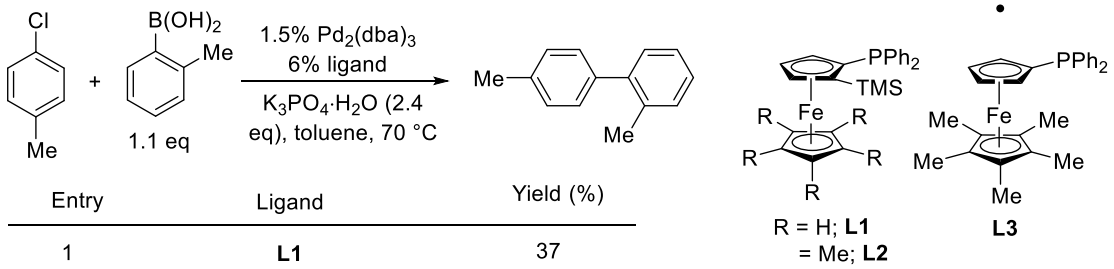


Figure 8. Prices of alkylphosphine and N-heterocyclic carbene ligands.

This limitation can be addressed by developing ligands from readily available and cost-effective materials. Aryl phosphines, which are typically less expensive than NHC carbenes and alkyl phosphines, offer a promising alternative. Triarylphosphine ligands, in particular, could be highly advantageous if they provide catalytic activity comparable to that of aryldialkylphosphine ligands. Various triarylphosphines have been documented in the literature for their effectiveness in coupling reactions involving chloroarenes.

4. Progress in Palladium Catalysts Featuring Sterically Bulky Triarylphosphine Ligands:

A notably mild and versatile method for the palladium-catalyzed cross-coupling of aryl chlorides using triarylphosphine ligands was first reported by Gregory C. Fu and colleagues in 2001[53]. They designed several ferrocene-derived arylphosphine ligands, labeled as **L1-L3**, and employed them in Suzuki-Miyaura coupling reactions with unactivated chloroarenes (Figure 9).



Entry	Ligand	Yield (%)
1	**L1**	37
2	**L2**	87
3	**L3**	8
4	PPh_3	<2

Figure 9. Application of riarylphosphines **L1-L3** as ligands in Suzuki reactions of aryl chlorides.

These findings underscore the crucial role of the TMS (trimethylsilyl) group in improving the reactivity of **L2**. At the same time, Richards *et al.* demonstrated a Suzuki coupling reaction using a ferrocene-based hindered ligand with palladium, achieving favorable yields with both activated an aryl chloride (4-chloronitrobenzene) and an unactivated aryl chloride (4-chlorotoluene[54].

Stockland *et al.* synthesized a triarylphosphine ligand (**L4**) with chlorine groups attached to the ortho positions of two of the phenyl rings of Ph_3P[55]. This ligand, **L4**, has proven effective in facilitating the activation of C-Cl bonds in both electron-donating and electron-withdrawing aryl chlorides (Figure 10). Although the ligand **L4** effectively catalyzed the coupling reactions, the exact role of the chlorine substituent in the ligand was not fully understood. The reduced basicity of the phosphine, caused by the electron-withdrawing effect of the chlorine atoms, along with the larger cone angle, may enhance the formation of a coordinatively unsaturated palladium species, thereby facilitating the initial oxidative addition step. Another possibility is the intramolecular oxidative addition of the C_6H_4-Cl bond of the ligand to palladium, leading to the formation of a four-membered palladacycle that could catalyze the reaction. Here it is important to note that the motif of Ligand **L4** can be compared to the Hartwig-type biphenyl-phosphine.

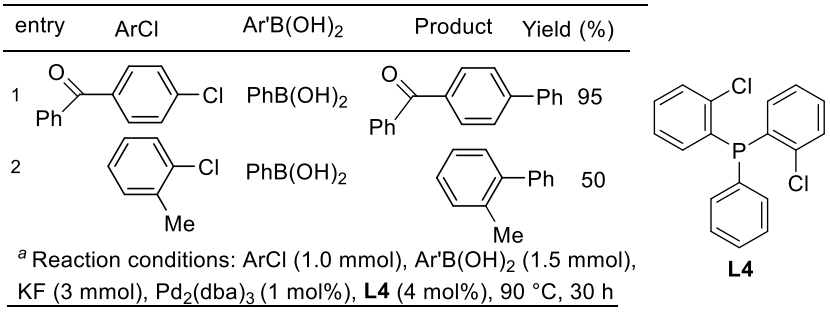


Figure 10. Application of **L4** in Suzuki coupling of aryl chlorides.

In 2004, Kwong *et al.* introduced air-stable and highly efficient ferrocene based triarylphosphine ligand (**L5**) and demonstrated its efficacy in the palladium-catalyzed Suzuki-Miyaura coupling of chloroarenes[56]. Notably, ligand **L5** enabled successful cross-coupling of chloroarenes with alkylboronic acids, which are typically challenging substrates (Figure 11).

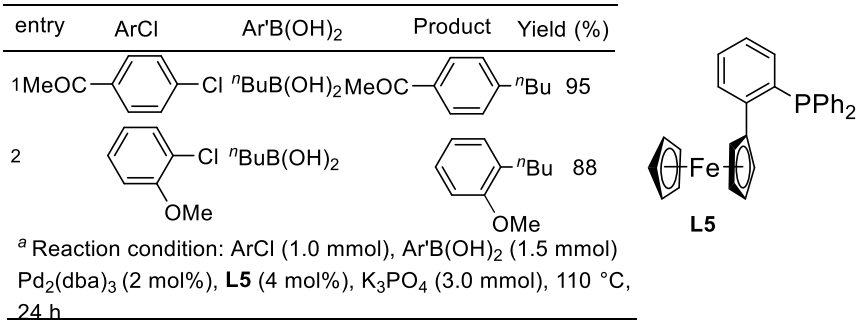
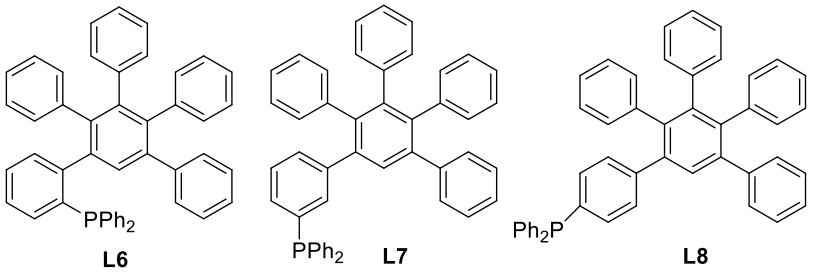
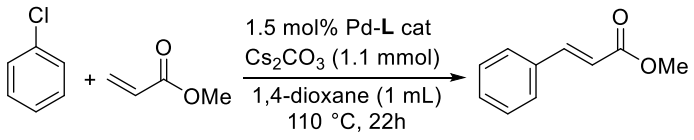


Figure 11. Application of **L5** in Suzuki coupling of aryl chlorides.

In 2006, Tsuji introduced a number of ligands featuring a 2,3,4,5-tetraphenylphenyl group (TPPh) attached to one of the phenyl rings of triarylphosphines, specifically in ortho- (**L6**), meta- (**L7**) and para-position (**L8**)[57]. Among these, ligand **L6** demonstrated exceptional efficiency in facilitating the use of nonreactive chloroarenes in various palladium-catalyzed reactions, including Mizoroki-Heck and Suzuki-Miyaura couplings (Figure 12).





entry	phosphine	yield (%)
1	**L6**	>99
2	**L7**	0
3	**L8**	0

Figure 12. Application of **L6 – L8** in Heck coupling of aryl chlorides.

To understand why **L6** exhibits remarkable efficiency in catalytic reactions, stoichiometric reactions of **L6** with $Pd(dba)_2$ has been performed at 50°C in THF, followed by the addition of maleic anhydride[58]. The resulting complex has been crystallized from a pentane/THF mixture. X-ray crystallography revealed that palladium in the complex forms a η^2-coordination with one of the phenyl rings of the TPPh moiety. This η^2 coordination is uniquely possible with the ortho-derivatives (**L6**). In contrast, the meta- (**L7**) and para- (**L8**) derivatives do not exhibit this η^2-coordination, which limits their catalytic activity. During catalytic reactions, the intramolecular η^2-coordination initially stabilizes the mono-phosphine species. However, this coordination can be disrupted by the substrate, facilitating the formation of highly unsaturated and catalytically active Pd(0) species. Similarly, Buchwald et al. observed that η^1-coordination stabilizes LPd(0) species. This unique η^2-coordination mode of **L6** with palladium explains its exceptional efficiency in catalyzing reactions involving unactivated aryl chlorides in Suzuki-Miyaura and Mizoroki-Heck reactions.

In this context, the ligand diphenyl(2',4',6'-triisopropylbiphenyl-2-yl)phosphine (**L9**), synthesized by Buchwald *et al.*, is particularly noteworthy[59]. Ligand **L9** has shown efficiency comparable to that of the alkylphosphine ligands developed by this group. (Figure 13).

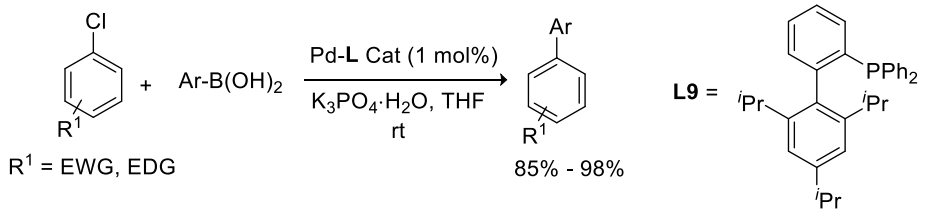


Figure 13. Application of ligand **L9** in Suzuki coupling of aryl chlorides.

Sarkar *et al.* introduced a new ligand, 1,3-diphenylphosphinoindole (**L10**), which has proven effective in palladium-catalyzed Suzuki-Miyaura reactions (Figure 14)[60]. Further study disclosed that the ligand functions in a monodentate mode and derivatives of 3-(diphenylphosphino)indole have been identified as a promising group of ligands. The donor properties and catalytic efficiency of the phosphino group have been influenced by the nature of the N-substituent on the indole ring. Additionally, a correlation between the chemical shift of the ^{31}P nucleus and the observed reactivity supports these findings.

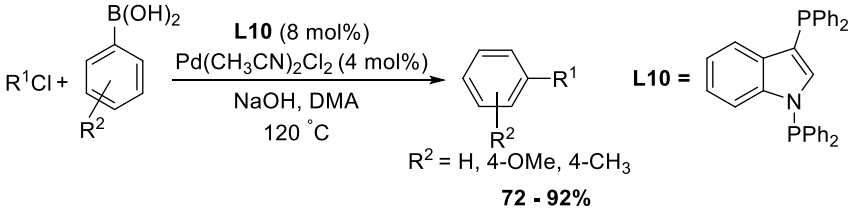


Figure 14. Application of ligand **L10** in Suzuki coupling of aryl chlorides.

The same group reported a series of aryldiphenylphosphino ligands derived from 1-aryl-pyrazole/pyrrole and applied them for the activation of chloroarenes (Figure 15)[61]. They also conducted a comparative study on the electronic and steric effects of phosphine ligands within a structurally alike biaryl motif, focusing on their performance in palladium-catalyzed Suzuki-Miyaura and Hiyama coupling reactions involving aryl chlorides. Their findings led to the following conclusions: (a) an optimal steric environment around phosphorus in triarylphosphines can make a ligand as efficient as its aryldialkyl counterpart, and (b) the involvement of a hemilabile spectator donor atom in the ligand does not necessarily enhance catalytic performance.

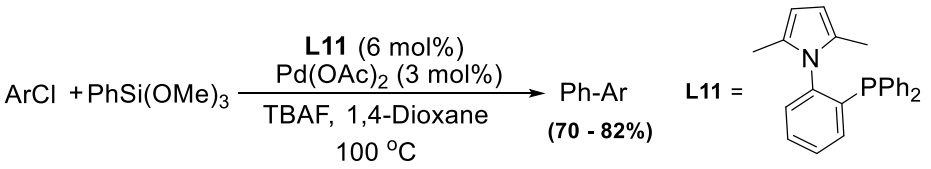


Figure 15. Application of ligand **L11** in Hiyama coupling reactions of aryl chlorides.

Sarkar *et al.* also developed bidentate P,N-P ligands based on indole (L12) and used them to catalyze the activation of aryl, heteroaryl, and benzyl chlorides in palladium-catalyzed Suzuki-Miyaura cross-coupling, and Buchwald-Hartwig amination reactions (Figure 16)[62-64].

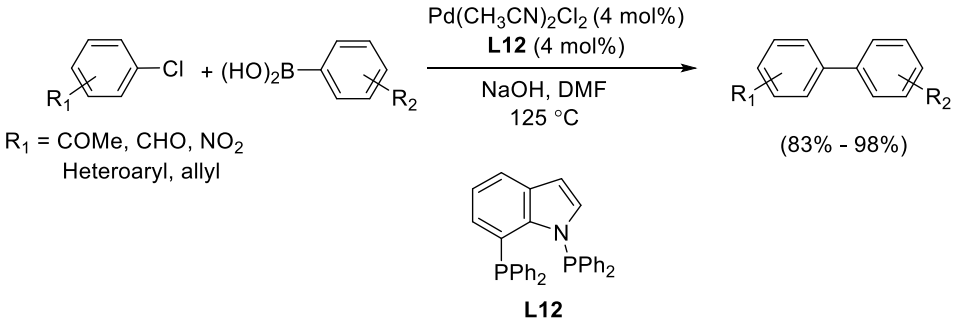


Figure 16. Application of ligand **L12** in Suzuki-Miyaura coupling reactions of aryl chloridesWhile Sarkar *et al.* were synthesizing bidentate ligands and exploring their applications, Kwong *et al.* developed another indolylphosphine ligand, **L13**[65]. The Pd/PPh_2-indole-phos system was found to effectively catalyze both borylation and Suzuki-Miyaura coupling reactions sequentially in a one-pot process, facilitating the direct synthesis of biaryl compounds with excellent yields. (Figure 16).

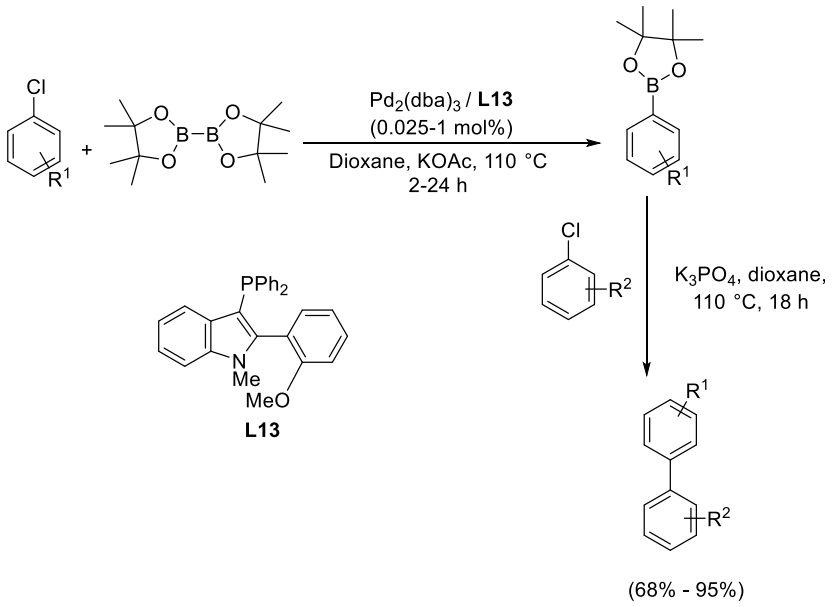


Figure 17. Pd-Catalyzed sequential borylation and Suzuki-Miyaura coupling in a one-pot process Using Ligand **L12.**

Lee *et al.* synthesized a highly ordered mesoporous polymer-supported diarylphosphine ligand (Meso-PPh_2 **; L14)** through a straightforward substitution reaction (Figure 17)[66]. The rigid polymer surface could inhibit the formation of bis-ligated palladium by restricting the flexibility of the polymer chain, thereby promoting the selective formation of highly reactive mono-ligated palladium without the need for an electron-rich ligand. Using this ligand, they effectively carried out the Suzuki-Miyaura cross-coupling of a range of aryl chlorides at room temperature, achieving high yields. Balakrishna *et al.* synthesized triazole-based triphenylphosphine ligands and used them for palladium-catalyzed cross-coupling reaction of aryl chlorides[67].

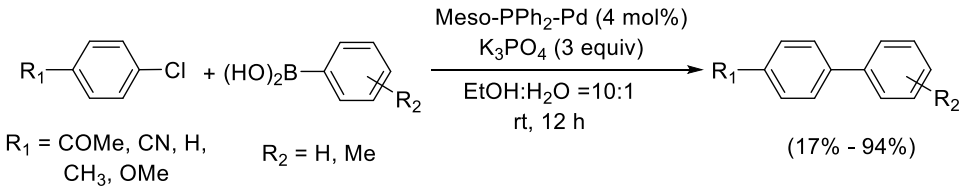


Figure 18. Highly ordered mesoporous polymer-supported diarylphosphine ligand for Pd-catalyzed Suzuki-Miyaura cross coupling of aryl chloride.

5. Conclusions

Despite significant advancements, several challenges persist in the field of catalytic coupling reactions involving aryl chlorides. While aryl chlorides offer cost advantages compared to other coupling partners, achieving comparable turnover numbers and ensuring cost-effectiveness of catalysts remain critical issues. Many pioneering studies have employed relatively high catalyst loadings, which may not be practical for industrial applications without achieving higher turnover numbers and frequencies.

Additionally, further experimental and theoretical research is needed to fully elucidate reaction mechanisms. Such insights are vital for the design of ligands tailored for the activation of challenging carbon-chlorine bonds. We hope this review encourages ongoing research and innovation in this vital area of catalysis.

6. Acknowledgements

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7. References

1. Schmidt, N. G.; Eger, E.; Kroutil, W. *ACS Catal.* **2016**, *6*, 4286. https://doi.org/10.1021/acscatal.6b00758
2. Brahmachari, G. *RSC Adv.* **2016**, *6*, 64676. https://doi.org/10.1039/C6RA14399G
3. Nagaraju, K.; Suresh, M.; Sreekantha, B. J. *Curr. Org. Chem.* **2019**, *23*. 3154. http://dx.doi.org/10.2174/1385272823666191202105820
4. Zhao, H. *RSC Adv.* **2024**, *14*, 25932. https://doi.org/10.1039/D4RA03885A
5. Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. Angew Chem. Int. Ed. **2005**, 44, 4442. https://doi.org/10.1002/anie.200500368
6. Castilo, -R, P.; Buchwald, S. *Chem. Rev.* **2016**, *116*, 12564. https://doi.org/10.1021/acs.chemrev.6b00512
7. Kanchana, U. S.; Diana, E. J.; Mathew, T. V.; Anilkumar, G. *Chemistry Select.* **2021**, *6*, 1579.

https://doi.org/10.1002/slct.202004433
8. Suzuki, A. *Chem. Rev*. **1995**, *95*, 2457. https://doi.org/10.1021/cr00039a007
9. Nicolaou, K. C.; Sorensen, E. J. *Classics in Total Synthesis*, VCH: New York, 1996, Chap. *31*.
10. Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11. https://link.springer.com/book/10.1007/3-540-45313-X
11. *Metal-catalyzed Cross-Coupling Reactions*, Vol. 2 Eds.: A. de Meijere, F. Diederich, Wiley-VCH: Weinheim, 2004.
12. Matsuoka, W.; Harabuchi, Y.; Nagata, Y.; Maeda, S. *Org. Bimol. Chem.* **2023**, *21*, 3132. https://doi.org/10.1039/D3OB00398A
13. D'Alterio, M. C.; Casals-Cruanas, E.; Tzours, N. V.; Talarico, G.; Nolan, S. P.; Poater, A. *Chem. Eur. J.* **2021**, *27*, 13481. https://doi.org/10.1039/D3OB00398A
14. Ng, S. S.; Pang, W. H.; Yuen, O. Y.; So, C. M. *Org. Chem. Front.* **2023**, *10*, 4408. https://doi.org/10.1039/D3QO00640A
15. Dong, D. –Q.; Yang, H.; Zhou, M, -Y.; Wei, Z. –H.; Wu, P.; Wang, Z. –L. *Curr. Opin. Green Sustain. Chem.* **2023**, *40*, 100778. https://doi.org/10.1016/j.cogsc.2023.100778
16. Sivakumar, S.; Aneeja, T.; Anilkumar, G. *Arkivoc*. **2022**, *viii*, 295. https://doi.org/10.24820/ark.5550190.p011.845
17. Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics*. **1992**, *11*, 3009. https://doi.org/10.1021/om00045a012
18. Amatore, C.; Carre, E.; Jutand, A.; M'Barki, M. A. *Orgametallics.* **1995**, *14*, 1818. https://doi.org/10.1021/om00004a039
19. Christmann, U.; Vilar, R. *Angew. Chem., Int. Ed*. **2005**, *44*, 366. https://doi.org/10.1002/anie.200461189
20. Molander, G. A.; Canturk, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9240. https://doi.org/10.1002/anie.200904306
21. Xue, L.; Lin, Z. *Chem. Soc. Rev.* **2010**, *39*, 1692. https://doi.org/10.1039/B814973A
22. Hansen, T.; Sun, X.; Tiezza, M. D.; Zeist, W.-J. V.; Poater, J, Hamlin, T. A.; Bockelhaupt, F. M. *Chem, Eur. J*. **2022**, *28*, e202103953. https://doi.org/10.1002/chem.202201093
23. Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed*. **2002**, *41*, 4176. https://doi.org/10.1002/1521-3773(20021115)41:22%3C4176::AID-ANIE4176%3E3.0.CO;2-U
24. Longcake, A.; Less, M. R.; Senn, M. S.; Chaplin, A. B. *Organometallics.* **2022**, *41*, 3557. https://doi.org/10.1021/acs.organomet.2c00400
25. Hooper, M. W.; Utsunomiya, M.; Hartwig, J. F. *J. Org. Chem.* **2003**, *68*, 2861. https://doi.org/10.1021/jo0266339
26. Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *Angew. Chem*. **2003**, *115*, 3818; *Angew. Chem., Int. Ed*. **2003**, *42*, 3690. https://doi.org/10.1002/anie.200351325
27. Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem*. **2002**, *219*, 131. https://link.springer.com/chapter/10.1007/3-540-45313-X_5
28. Walker, S. D.; Cowley, A.; Hii, K. K.; Jutand, A. *Angew. Chem*. **2002**, *114*, 1838; *Angew. Chem., Int. Ed*. **2002**, *41*, 1760. https://doi.org/10.1002/1521-3773(20020517)41:10%3C1760::AID-ANIE1760%3E3.0.CO;2-3

29. Firsan, S. J.; Sivakumar, V.; Colacot, T.J. *Chem. Rev.* **2022**, *122*, 16983. https://doi.org/10.1021/acs.chemrev.2c00204
30. Shaughnessy, K. H. *Isr. J. Chem.* **2020**, *60*, 180. https://doi.org/10.1002/ijch.201900067
31. Galardon, E.; Ramdeehul, S.; Brown, J. M.; Cowley, A.; Hii, K. K.; Jutand, A. *Angew. Chem.* **2002**, *114*, 1838; *Angew. Chem., Int. Ed.* **2002**, *41*, 1760. https://doi.org/10.1002/1521-3773(20020517)41:10%3C1760::AID-ANIE1760%3E3.0.CO;2-3
32. Stambuli, J. P.; Buehl, M.; Hartwig, J. F. *J. Am. Chem. Soc*. **2002**, *124*, 9346. https://doi.org/10.1021/ja0264394
33. Stambuli, J. P.; Incarvito, C. D.; Buehl, M.; Hartwig, J. F. *J. Am. Chem. Soc*. **2004**, *126*, 1184. https://doi.org/10.1021/ja037928m
34. Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3387. https://doi.org/10.1002/(SICI)1521-3773(19981231)37:24%3C3387::AID-ANIE3387%3E3.0.CO;2-P
35. Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem*. **2002**, *67*, 5553. https://doi.org/10.1021/jo025732j
36. Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818. https://doi.org/10.1021/ja036947t
37. Zapf, A.; Jackstell, R.; Rataboul, F.; Riermeier, T.; Monsees, A.; Fuhrmann, C.; Shaikh, N.; Dingerdissen, U.; Beller, M. *Chem. Commun.* **2004**, 38. https://doi.org/10.1039/B311268N
38. Harkal, S.; Rataboul, F.; Zapf, A.; Fuhrmann, C.; Riermeier, T.; Monsees, A.; Beller, M. *Adv. Synth. Catal.* **2004**, *346*, 1742. https://doi.org/10.1002/adsc.200404213
39. So, C. M.; Lau, C. P.; Chan, A. S. C.; Kwong, F. Y. *J. Org. Chem.* **2008**, *73*, 7731. https://doi.org/10.1021/jo8014819
40. So, C. M.; Lau, C. P.; Kwong, F. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 8059. https://doi.org/10.1002/anie.200803193
41. Kantchey, E. A. B.; Brien, C. J. O.; Organ, M.G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. https://doi.org/10.1002/anie.200601663
42. Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440. https://doi.org/10.1021/ar800020y
43. Titcomb, L. R.; Caddick, S.; Cloke, F. G. N. Wilson, D. J.; McKerrecher, D. *Chem. Commun*. **2001**, 1388. https://doi.org/10.1039/B104297C
44. Sar, V. C.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics*. **2002**, *21*, 5204. https://doi.org/10.1021/om020608b
45. Viciu, M. S.; Germaneau, R. F.; Navarro, O.; Stevens, E. D.; Nolan, S. P. *Organometallics.* **2002**, *21*, 5470. https://doi.org/10.1021/om020804i
46. Viciu, M. S.; Kelly, R. A.; Stevens, E. D.; Naud, F. Studer, M.; Nolan, S. P. *Org. Lett*. **2003**, *5*, 1479. https://doi.org/10.1021/ol034264c
47. Navarro, O.; Marion, N.; Scott, N. M.; Gonz, J.; Jez, D.; Amoroso, Bell, A.; Nolan, S. P. *Tetrahedron.* **2005**, *61*, 9716. https://doi.org/10.1016/j.tet.2005.06.081
48. Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101. https://doi.org/10.1021/ja057704z

49. Jackstell, R.; Andreu, M. G. ; Frisch, A.; Selvakumar, K.; Zapf, A.; Klein, H.; Spannenberg, A.; Rottger, D.; Briel, O.; Karch, R.; Beller, M. *Angew. Chem.* **2002**, *114*, 1028; *Angew. Chem. Int. Ed.* **2002**, *41*, 986. https://doi.org/10.1002/1521-3773(20020315)41:6%3C986::AID-ANIE986%3E3.0.CO;2-M
50. Brien, C. J. O.; Kantchey, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. Eur. J.* **2006**, *12*, 4743. https://doi.org/10.1002/chem.200600251
51. Schneider, S. K.; Herrmann, W. A.; Herdtweck, E. *J. Mol. Catal. A.* **2006**, *245*, 248. https://doi.org/10.1016/j.molcata.2005.08.046
52. Organ, M. G.; Chass, G. A.; Fang, D. –C.; Hopkins, A. C.; Valente, C. *Synthesis.* **2008**, 2776. http://doi.org/10.1055/s-2008-1067225
53. Liu, S-. Y.; Choi, M. J.; Fu, G. C. *Chem. Commun*. **2001**, 2408. https://doi.org/10.1039/B107888G
54. Pickett, T. E.; Richards, C. J. *Tetrahedron Lett.* **2001**, *42*, 3767. https://doi.org/10.1016/S0040-4039(01)00568-8
55. Pramick, M. R.; Rosemeier, S. M.; Beranek, M. T.; Nickse, S. B.; Stone, J. J.; Stockland, Jr. R. A.; Baldwin, S. M.; Kastner, M. E. *Organometallics*. **2003**, *22*, 523. https://doi.org/10.1021/om020885i
56. Kwong, F. Y.; Chan, K. S.; Yeung, C. H.; Chan, A. S. C. *Chem. Commun*. **2004**, 2336. https://doi.org/10.1039/B407661C
57. Iwasawa, T.; Komano, T.; Tajima, A.; Tokunaga, M.; Obora, Y.; Fujihara, T.; Tsuji, Y. *Organometallics*. **2006**, *25,* 4665. https://doi.org/10.1021/om060615q
58. Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed*. **2004**, *43*, 1871. https://doi.org/10.1002/anie.200353615
59. Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc*. **2005**, *127*, 4685. https://doi.org/10.1021/ja042491j
60. Saha, D.; Ghosh, R.; Sarkar, A. *Tetrahedron*, **2013**, *69*, 3951. https://doi.org/10.1016/j.tet.2013.03.030
61. Saha, D.; Ghosh, R; Mandal, A. K.; Sarkar, A. *J. Organomet. Chem.*, **2015**, *776*, 89. https://doi.org/10.1016/j.jorganchem.2014.11.008
62. Ghosh, R.; Adarsh, N. N.; Sarkar, A. *J. Org. Chem.* **2010***, 75*, 5320. https://doi.org/10.1021/jo100643j
63. Ghosh, R.; Sarkar, A. *J. Org. Chem.* **2010**, *75*, 8283. https://doi.org/10.1021/jo1016458
64. Ghosh, R.; Sarkar, A. *J. Org. Chem.* **2011**, *76*, 8508. https://doi.org/10.1021/jo2014438
65. Chow, W. K.; Yuen, O. Y.; So, C. M.; Wong, W. T.; Kwong, F. Y. *J. Org. Chem*. **2012**, *77*, 3543. https://doi.org/10.1021/jo202472k
66. Kim, H. S.; Lee, H. –Y.; Joung, S. *Asian J. Org. Chem.* **2024**, *13*, *e203400011*. https://doi.org/10.1002/ajoc.202400011
67. Kote, B. S.; Mohlte, M. A.; Mondal, D.; Pandey, M. K. Balakrishna, M. S. *Eur. J. Inorg. Chem.* **2023**, *26*, *e202300291*. http://doi.org/10.1002/ejic.202300291

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