



Review

Bulky-Yet-Flexible Carbene Ligands and Their Use in Palladium Cross-Coupling

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Abstract: In recent years, several classes of new *N*-heterocyclic carbene (NHC) ligands were developed around the concept of “flexible steric bulk”. The steric hindrance of these ligands brings stability to the active species, while ligand flexibility still allows for the approach of the substrate. In this review, the synthesis of several types of new classes, such as **IBiox**, cyclic alkyl amino carbenes (**CAAC**), **ITent**, and **IPr*** are discussed, as well as how they move the state-of-the-art in palladium catalyzed cross-coupling forward.

Keywords: *N*-heterocyclic carbenes; flexible sterics; palladium; cross-coupling

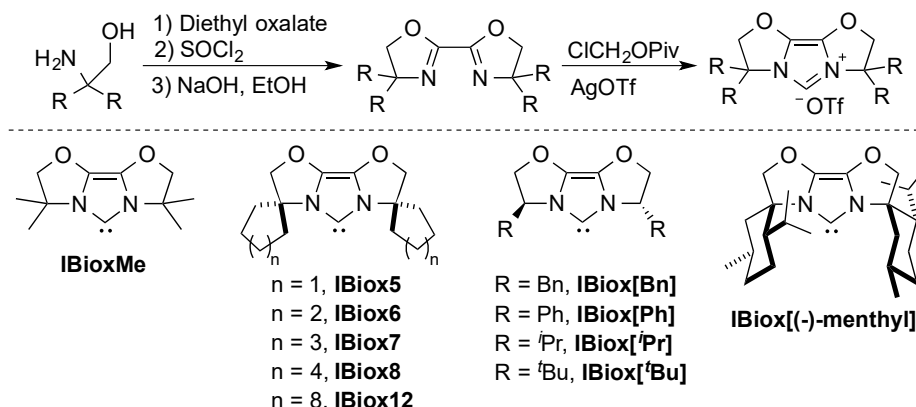
1. Introduction

In recent years, interest on *N*-heterocyclic carbenes (NHCs) has been growing rapidly due to their excellent stability, diversity and a possible tunability of steric and electronic properties [1–13]. Fine-tuning the steric hindrance led to major breakthroughs and improvements in catalysis [14–17]. Bulkier ligands stabilize the active species and disfavor bimolecular decomposition and other routes of deactivation [18–21]. However, steric bulk disfavors the approach of the substrate, which might diminish catalytic activity. Therefore, a delicate balance between skeletal flexibility and steric bulk is required to enhance catalytic efficacy [18–22].

The focus of this review is on three different classes of bulky ligands: **IBiox** [23], cyclic alkyl amino carbenes (**CAAC**) [24] and *N,N'*-bis(aryl)imidazolylienes (such as the **ITent**-, **IPr***- and **SICyoctNap** series) [25–29]. Their synthesis is discussed, as well as their role in palladium-catalyzed cross-coupling reactions.

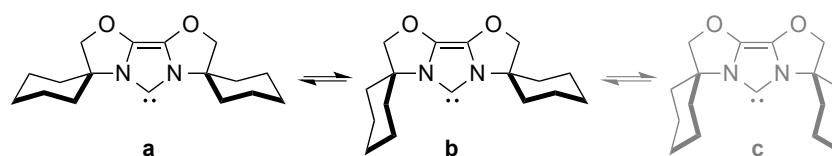
2. IBiox

Glorius was the first to report on the concept of “flexible steric bulk” with his work on bisoxazoline-derived *N*-heterocyclic carbene ligands (**IBiox**) [23,30]. The rigidity of these ligands comes from their tricyclic backbone. These ligands can be easily prepared, starting from their corresponding bisoxazolines [15,23,30] and tuning of steric bulk, flexibility, and chirality can be achieved by judicious substitutions [31,32] (Scheme 1).



Scheme 1. Synthesis of the **IBiox** ligand series [23,30,32–34].

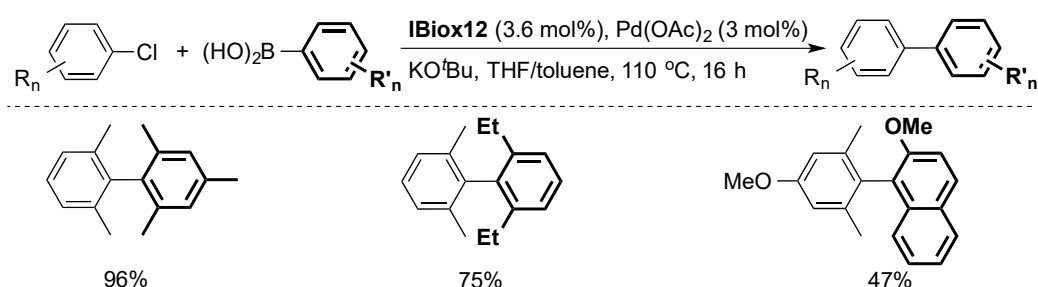
The flexibility of the steric hindrance of these ligands can be demonstrated by the equilibrium between various conformers of **IBiox6** (Scheme 2) [30].



Scheme 2. Equilibrium between conformations of **IBiox6** (a–c) [30].

2.1. Suzuki–Miyaura Cross-Coupling

The steric flexibility of the **IBiox** series proved to be an important factor in enabling challenging cross-coupling reactions, such as the formation of *ortho*-substituted biaryls via a Suzuki–Miyaura coupling [15,23,30]. Screening of a series of **IBiox** ligands with cycloalkyl substituents showed that the formation of highly hindered tetra-*ortho*-substituted biaryls requires increased steric hindrance about the NHC ligand [23]. In that context, **IBiox12** emerged as the desired catalyst for this reaction (Scheme 3) [23].



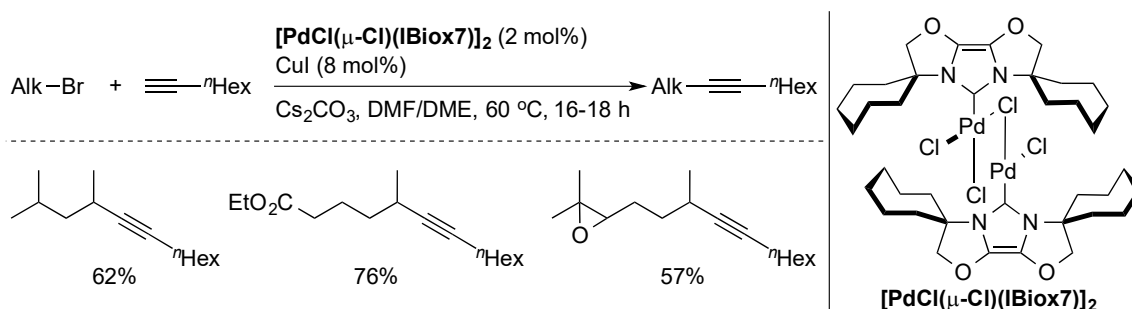
Scheme 3. Selected examples of Suzuki–Miyaura cross-coupling using **IBiox12** [23].

While this system is produced in situ, the well-defined **IBiox12**-based dimer $[\text{PdCl}(\mu\text{-Cl})(\text{IBiox12})]_2$ was subsequently isolated. The latter showed comparable results to its in situ counterpart in cross-coupling reactions [23].

2.2. Alkyl Sonogashira Cross-Coupling

The Sonogashira cross-coupling [14,35,36] of alkynes with organic halides is an efficient method of obtaining functionalized alkynes. However, aromatic halides are typically used. Coupling of non-activated alkyl halides was always elusive due to problematic oxidative addition steps and side-reactions such as β -hydride elimination. The first successful example of this reaction [37] was the

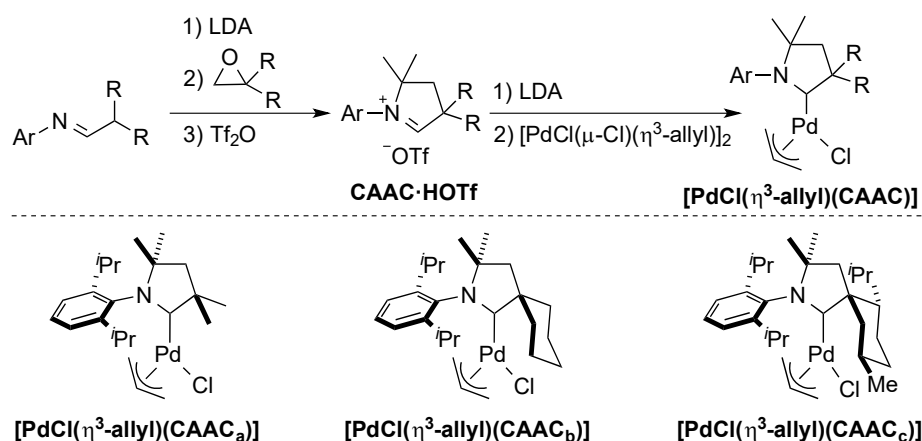
palladium-catalyzed coupling of primary alkyl halides with terminal alkynes by Fu and co-workers. Later, the first Sonogashira coupling of secondary bromides with 1-octyne was developed by Glorius and co-workers [38], using the well-defined $[\text{PdCl}(\mu\text{-Cl})(\text{IBiox7})]_2$ pre-catalyst (Scheme 4).



Scheme 4. Selected examples of Sonogashira coupling using a well-defined Pd-IBiox complex [38].

3. CAAC Series

Bertrand and co-workers recognized the concept of sterically flexible ligands in their development of the novel class of cyclic (alkyl)(amino)carbenes (CAACs) [24,39,40]. These electron-rich ligands are pyrrolidine-based and bear two quaternary carbons. They are prepared from the corresponding imines [24] and after deprotonation of the CAAC·HOTf, under harsh conditions, using LDA (lithium diisopropylamide), addition of palladium allyl chloride dimer leads to the formation of the well-defined $[\text{PdCl}(\eta^3\text{-allyl})(\text{CAAC})]$ complex (Scheme 5).



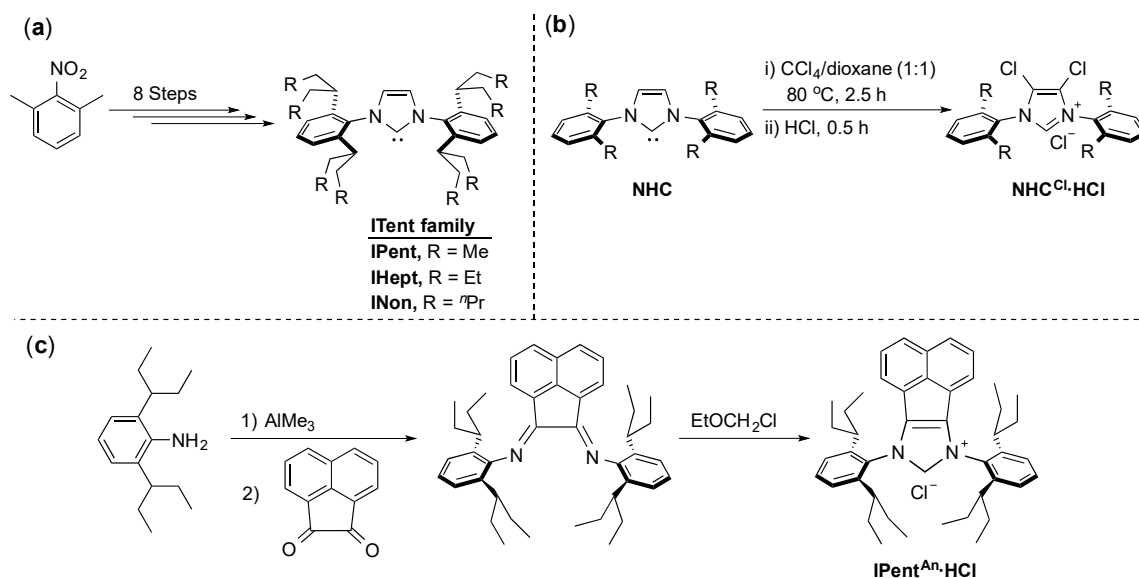
Scheme 5. Synthesis of the CAAC ligand series [24].

The reactivity of these $[\text{PdCl}(\eta^3\text{-allyl})(\text{CAAC})]$ complexes was tested in the α -arylation of aryl chlorides with phenylethylketone [24]. It was found that the most sterically demanding ligand (CAAC_c) was the most effective when using an unsubstituted aryl chloride, whereas the flexibility of CAAC_b led to higher yields with more sterically hindered aryl chlorides.

4. ITent

Recent studies showed that up to a certain point, there is a proportional relationship between the increase in the NHC steric bulk and the increase in catalytic activity [5,41]. This phenomenon led to the implementation of flexible bulk into the design of one of the most commonly used NHCs: IPr (*N,N'*-bis-[2,6-(di-*iso*-propyl)phenyl]imidazol-2-ylidene). This new series is known as ITent (after its tentacular structure) and the synthesis of these IPr-mimicking ligands was described by Nolan and co-workers (Scheme 6a) [42]. Analogues of these ligands with a chloro-substituted backbone were described by Organ and co-workers in their PEPPSI (Pyridine-Enhanced Precatalyst Preparation

Stabilization and Initiation) series [43] (Scheme 6b), and more recently, Liu and co-workers described the synthesis of the acenaphthyl-substituted backbone analogue **IPent^{An}** (Scheme 6c) [44].



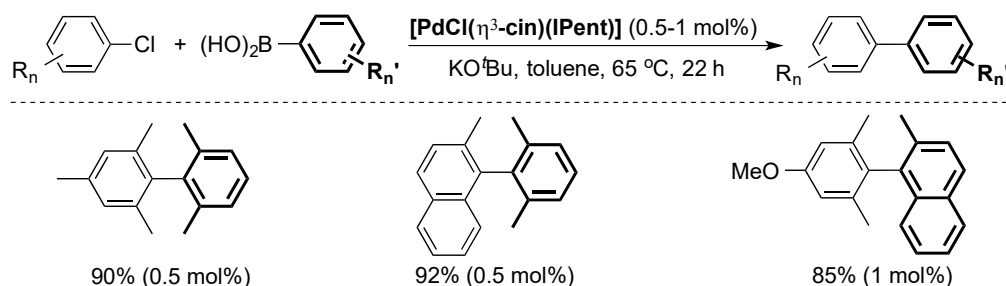
Scheme 6. Synthetic access to **ITent** ligands (a–c) [42–44].

The Nolan group used this **ITent** series for the synthesis of their “custom-made” pre-catalysts [**PdCl(η³-cin)(ITent)**] (cin = cinnamyl) and [**PdCl(acac)(ITent)**] (acac = acetylacetonate) [42], while Organ used them to further optimize the **PEPPSI** series [16,27].

4.1. Suzuki–Miyaura Cross-Coupling

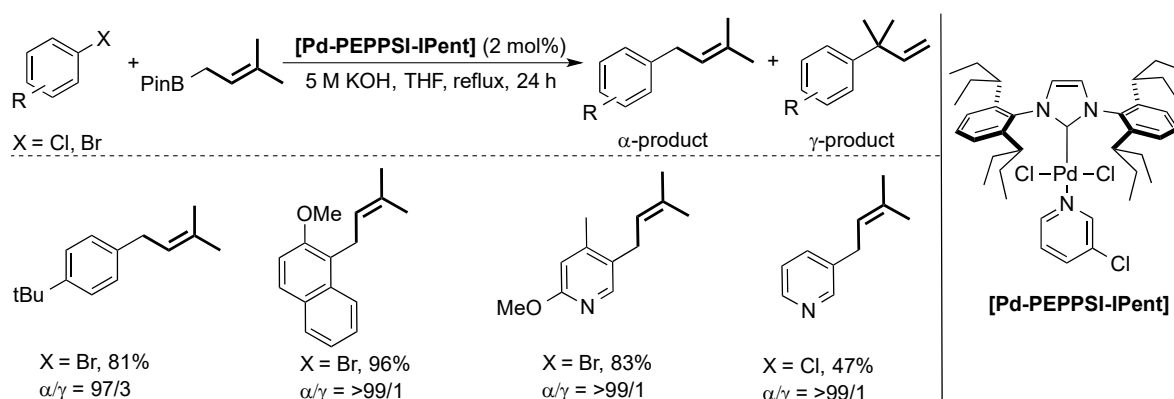
The synthesis of tetra-*ortho*-substituted biaryls under mild conditions remains a challenge in the Suzuki–Miyaura reaction. As shown above, the use of ligands with flexible bulk proved to be critical, and the first example using NHC ligands was described by Glorius in 2004 [23]. Organ was able to further optimize the reaction using the **ITent** series. More specifically, the well-defined **PEPPSI-IPent** pre-catalyst was used to achieve a wider scope than previous reports [27].

The Nolan group used the well-defined [**PdCl(η³-cin)(ITent)**] pre-catalyst series to further advance the state-of-the-art [42]. Of particular interest, [**PdCl(η³-cin)(IPent)**] was able to efficiently catalyze the cross-coupling of highly hindered aryl chlorides with boronic acids at low catalysts loading (Scheme 7).



Scheme 7. Selected examples of the Suzuki–Miyaura coupling using [**PdCl(η³-cin)(IPent)**] [42].

Organ and co-workers also used the [**Pd-PEPPSI-IPent**] pre-catalyst for the challenging coupling of allylboronic acid with different aryl halides [45]. In this context, (hetero)aryl halides were successfully coupled with high selectivity for the α-product (Scheme 8).

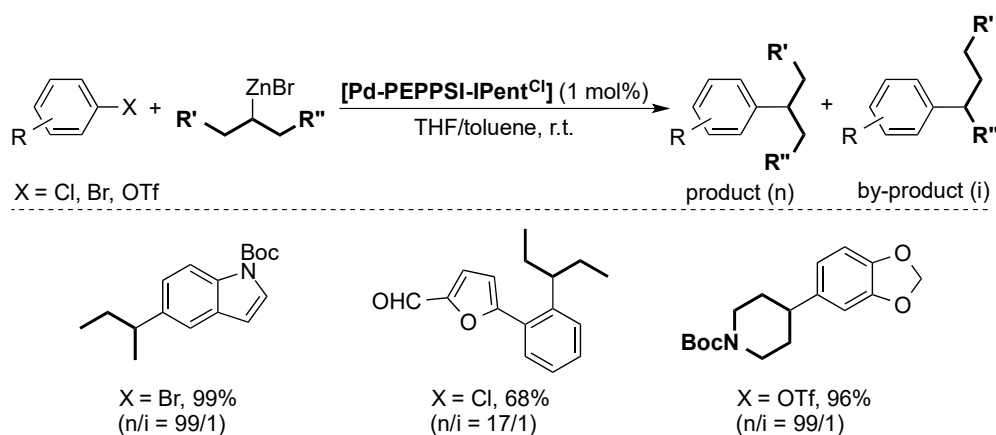


Scheme 8. Examples of the Suzuki–Miyaura coupling using allylboronic esters and aryl halides [45].

Recently, Liu and co-workers showed that the **[Pd-PEPPSI-IPent^{An}]** precatalyst is efficient in the the Suzuki–Miyaura coupling of a wide range of hindered arylboronic acids and hindered aryl chlorides at 80 °C using a 1 mol % Pd loading [44].

4.2. Negishi Cross-Coupling

After the first Negishi coupling with the well-defined **[Pd-PEPPSI-IPr]** pre-catalyst [46], the Organ group showed that the **[Pd-PEPPSI-IPent]** pre-catalyst was even more active, especially in the synthesis of tetra-*ortho*-substituted biaryls [47,48]. The same palladium pre-catalyst also proved to be highly efficient in the coupling of secondary alkylzinc substrates to aryl halides [49]. The flexible steric bulk of the **IPent** ligand reduced the β -hydride elimination/migratory insertion considerably, limiting the formation of the isomeric by-product. Later, Organ and co-workers improved this selectivity even further by using **[Pd-PEPPSI-IPent^{Cl}]** (Scheme 9) [43].

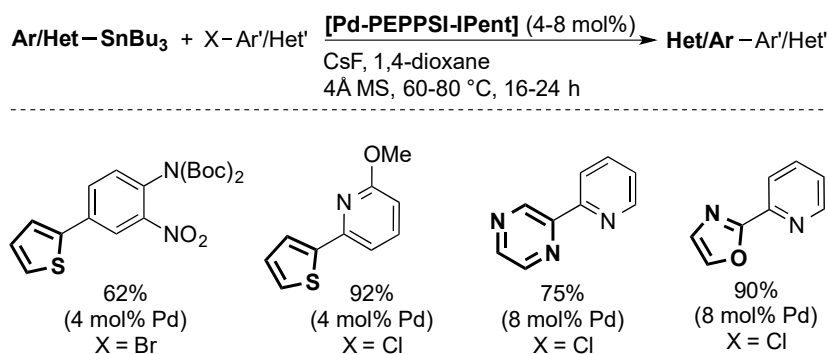


Scheme 9. Selected examples for the Negishi cross-coupling of secondary alkylzinc substrates [43].

Recently, Organ and co-workers described a silica-supported pre-catalyst, **[Pd-PEPPSI-IPent-SiO₂]**, and evaluated its activity in challenging Negishi cross-coupling reactions under flow conditions [50]. The catalyst material was used in a packed-bed reactor at room temperature and small residence times (10 min or less) were enough to obtain high conversions.

4.3. Stille Coupling

In 2010, Organ and co-workers reported a Stille coupling using **[Pd-PEPPSI-IPent]** (Scheme 10) [51]. While the method can be used for aryls and heteroaryl substrates, at relatively mild temperatures (60–80 °C), high catalyst loadings are needed in all cases (4–8 mol %).

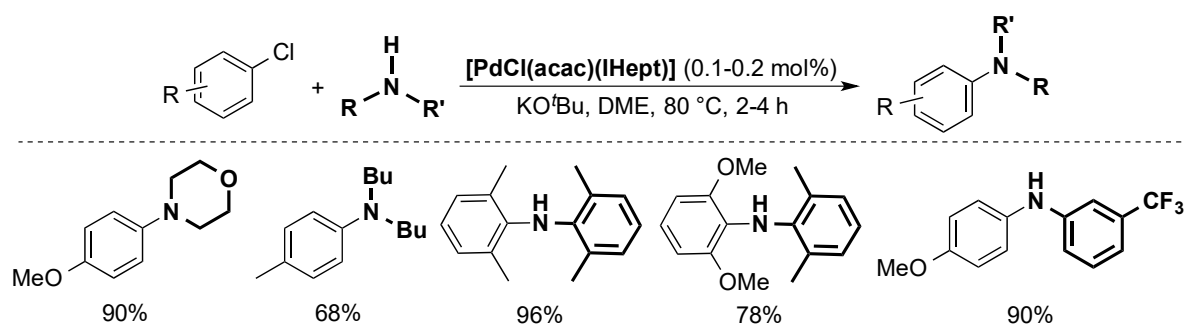


Scheme 10. Examples of the Stille coupling catalyzed by [Pd-PEPPSI-IPent] [51].

4.4. Buchwald-Hartwig Cross-Coupling

After the first report of the use of palladium-NHC systems for the amination reaction by Nolan [52], the concept of ligands with “flexible bulk” advanced the state-of-the-art. Organ reported the use of [Pd-PEPPSI-IPent] [53] under milder conditions than the ones used with the [Pd-PEPPSI-IPr] analogue, allowing for a greater tolerance of functional groups. The IPent derivative was even capable of catalyzing some reactions that were previously unattainable using the IPr-based catalyst [54]. However, it must be noted that high catalyst loadings (4 mol %) were necessary to achieve good results. More recently, the same group successfully achieved the coupling of various amides with aryl and heteroaryl chlorides using [Pd(η^3 -cin)Cl(DiMeIHept^{Cl})] as catalyst, assisted by boron-derived Lewis acids [55].

The Nolan group was able to reduce the catalyst loading by using [PdCl(acac)(IHept)] complexes (Scheme 11) [42]. More specifically, the use of the IHept ligand permitted to lower the catalyst loading to 0.1–0.2 mol %. This system allows for the use of otherwise difficult coupling partners, such as electron-poor anilines.



Scheme 11. Examples of the Buchwald-Hartwig coupling catalyzed by [PdCl(acac)(IHept)] [42].

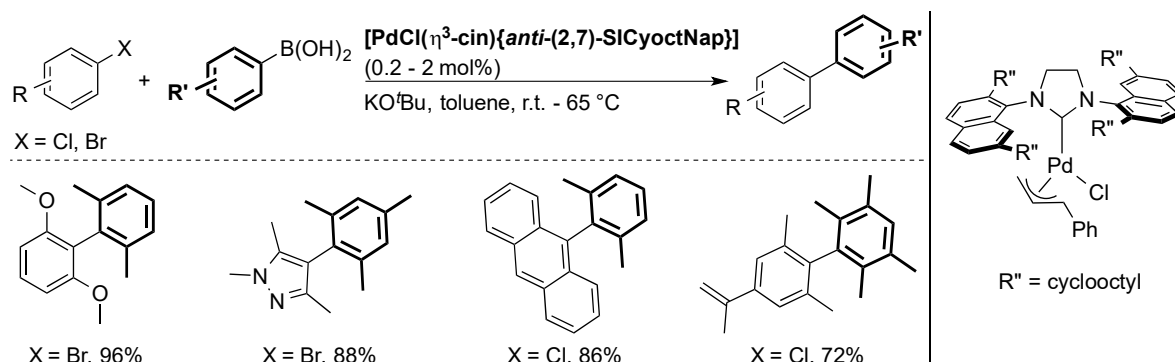
The Organ group investigated the coupling of 2-aminopyridine derivatives using [Pd-PEPPSI-IPent^{Cl}] [56]. Such catalysts were successful in the coupling of such aminopyridines with various aryl chlorides, but it must be mentioned that catalyst poisoning occurred due to metal coordination of the aminopyridine.

Recently, Liu and co-workers showed that [Pd-PEPPSI-IPent^{An}] was an efficient pre-catalyst in the amination of (hetero)aryl chlorides under aerobic conditions [57].

5. N-Naphthyl-Based NHCs

Another class of NHC ligands with naphthyl groups on the nitrogen atoms was synthesized by Dorta and co-workers and used to prepare well-defined palladium pre-catalysts [29,58–60]. [PdCl(η^3 -cin){*anti*-(2,7)-SiCyoctNap}], one of the most important complexes of the series, was the first well-defined complex to promote the coupling of tetra-*ortho*-substituted biaryls via a Suzuki–Miyaura

reaction at room temperature (Scheme 12) [29,60]. It showed that the success of this ligand lied with the NHC being twisted around the metal center with two bulky faces and two less hindered faces.



Scheme 12. Selected examples using $[\text{PdCl}(\eta^3\text{-cin})\{\text{anti-(2,7)-SiCyoctNap}\}]$ [29].

6. IPr* and Related NHCs

The **IPr*** ligand proved optimal for the balance between sterics and flexibility. This hindered ligand, which was first synthesized by Markó and co-workers [28], triggered interest and a number of congeners were developed [61–64]. Other manipulations of the **IPr** framework were investigated, such as the **IPr⁺C** series by Holland and co-workers [65] and the substitution of the NHC backbone with long alkyl chains by Glorius and co-workers [66] (Figure 1).

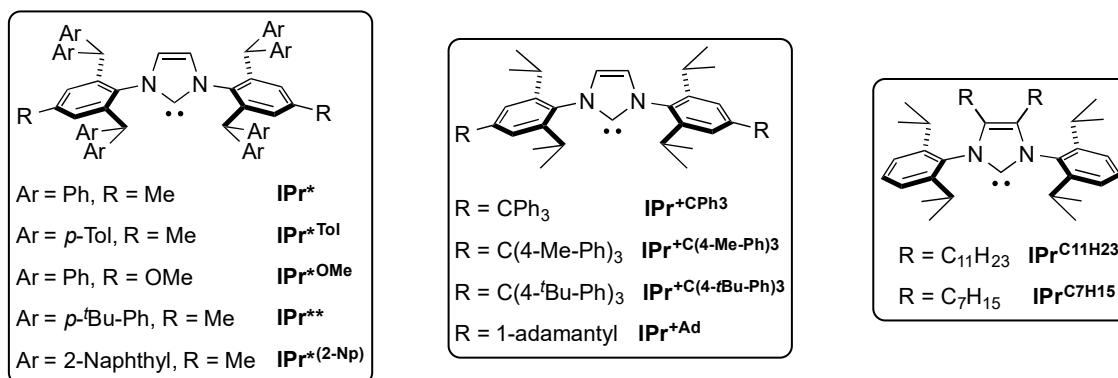
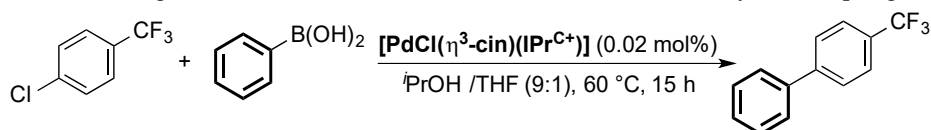


Figure 1. Structure of the **IPr***, **IPr⁺C** and **IPr^{CxHy}** ligands [28,61–64].

6.1. Suzuki Miyaura Cross-Coupling

The $[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^*)]$ pre-catalyst proved to be efficient in the preparation of tetra-*ortho*-substituted biaryls via Suzuki–Miyaura coupling at room temperature using 1 mol % Pd loading [67].

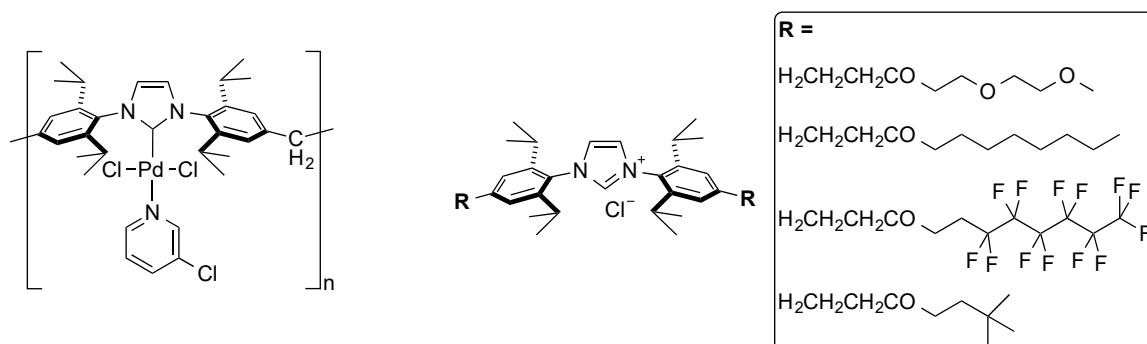
Holland and co-workers reported the $[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^+\text{C})]$ series in Suzuki–Miyaura coupling of 4-chloro(trifluoromethyl)benzene and phenylboronic acid [65]. When compared with the **IPr** analogue, all complexes were found more active with a trend of increase in steric bulk directly proportional to increase of activity up to a certain tipping point; this is where flexibility is compromised because of a too large steric hindrance (Table 1).

Table 1. Investigation of the $[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^{\text{C}+})]$ series in Suzuki–Miyaura coupling [65].


Entry	$[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^{\text{C}+})]$	GC Conversion (%)
1	$[\text{PdCl}(\eta^3\text{-cin})(\text{IPr})]$	55%
2	$[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^{\text{C}+\text{Ph}_3})]$	87%
3	$[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^{\text{C}+(4\text{-Me-Ph})_3})]$	86%
4	$[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^{\text{C}+(4\text{-}i\text{Bu-Ph})_3})]$	85%
5	$[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^{\text{C}+\text{Ad}})]$	69%

Recently, Qian and co-workers reported a polymer analogue to the IPr ligand (Figure 2, left) for use as a recoverable catalyst [68]. This catalyst was tested in the cross-coupling involving activated aryl bromides and chlorides. Reusability of the catalyst was shown over 6 runs—however, no kinetic data was provided—thus the possibility of the system acting as a reservoir of active species cannot be ruled out.

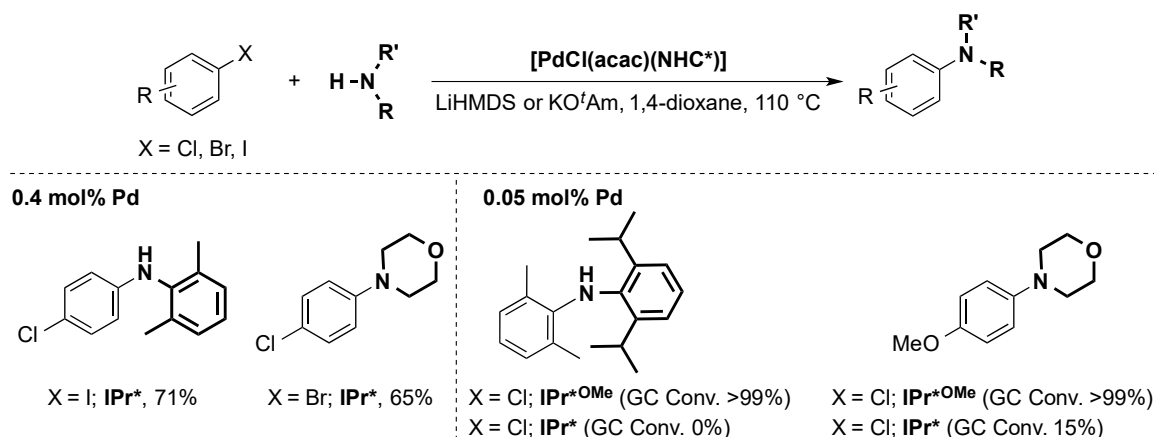
An alternative approach to catalyst separation using membranes was undertaken by Ormerod and co-workers on IPr and related ligands. While early studies were carried out on IPr ligand [69], modification of the latter by appending long chains at the *para*-position of the phenyl ring (Figure 2, right) proved judicious for catalyst recovery through nanofiltration. This allowed the cross-coupling reaction in a semicontinuous mode in a membrane-assisted reactor [70].

**Figure 2.** Polymer-modified IPr-complex (left) [68] and *para*-tailed IPr ligands (right) for semicontinuous reactions [70].

6.2. Buchwald Hartwig Cross-Coupling

The Nolan group investigated the use of $[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^*)]$ and $[\text{Pd-PEPPSI-IPr}^*]$ in the Buchwald–Hartwig reaction [71–73] and found that they were the most active pre-catalysts for this reaction to date. Both complexes showed similar activity, which indicates that the active species is the same in both cases. The $[\text{PdCl}(\eta^3\text{-cin})(\text{IPr}^*)]$ pre-catalyst was also used in a solvent-free amination using 1 mol % of the complex in neat condition [74]. This allowed for the use of primary amines at room temperature, which was previously not possible.

The very easily prepared $[\text{PdCl}(\text{acac})(\text{IPr}^*)]$ pre-catalyst was shown to be active in the same reaction [71] and showed chemoselective arylation of various dihalides resulting in mono-aminated products. $[\text{PdCl}(\text{acac})(\text{IPr}^*\text{OMe})]$ was also tested and proved to be even more active, allowing for the coupling of challenging electron-poor anilines (Scheme 13) [62].

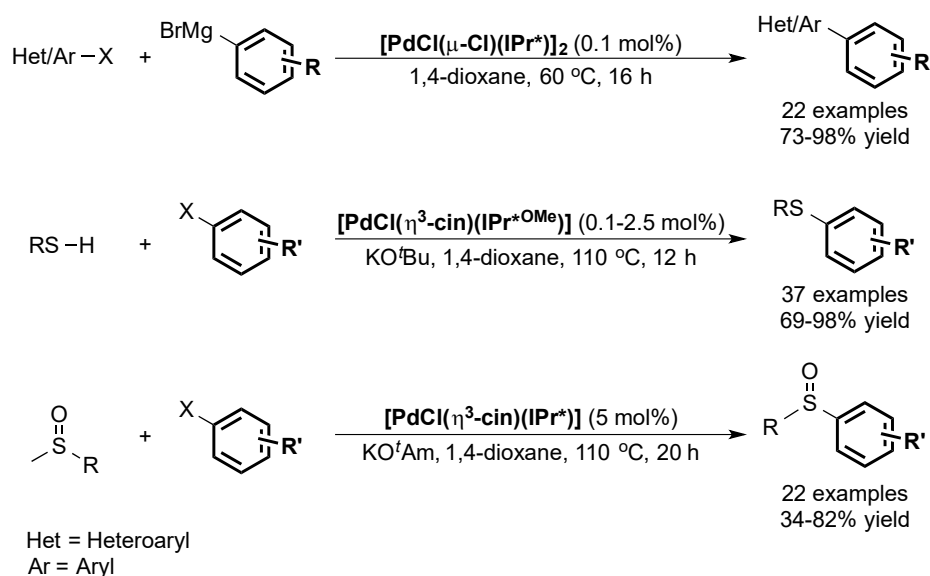


Scheme 13. Examples of the Buchwald-Hartwig coupling using $[\text{PdCl}(\text{acac})(\text{IPr}^*)]$ or $[\text{PdCl}(\text{acac})(\text{IPr}^*\text{OMe})]$ as pre-catalysts [62,71]. (KO^tAm = potassium *tert*-amylate).

Glorius and co-workers used their series of long-carbon-chain-based palladium complexes in the Buchwald-Hartwig amination [66]. Of this series, $[\text{PdCl}(\eta^3\text{-allyl})(\text{IPr}^{\text{C11H23}})]$ (see Figure 1) proved to be the most active (0.1 mol % Pd loading, 75 °C).

6.3. Other Palladium-Catalyzed Reactions

The **IPr*** ligand and its analogues were also used in the cross-coupling of Grignard reagents leading to the formation of tetra-*ortho*-substituted compounds [75] in high yields. Finally, the same ligand family was shown to lead to active catalysts in the formation of C–S bonds (Scheme 14) [76,77].



Scheme 14. Other palladium-catalyzed cross-couplings using **IPr*** and **IPr*OMe** ligands [75–77].

7. Conclusions and Outlook

“Bulky yet flexible” ligands were recently investigated, greatly advancing the state-of-the-art, particularly in reactions involving sterically congested coupling partners. The correlation between flexible steric bulk and catalytic activity is not always straightforward, as is proven by the failure of some extremely large ligands.

Advancements in this field not only benefited palladium chemistry but were also successfully applied to other research areas and related metals such as nickel. Various reports on the design and applications of **IPr**- and **IPr***-based (among other related derivatives) nickel catalysts by Nolan [78–81],

Nakamura [82], Ackermann [83], Sun [84], Cramer [85], Newman [86], and Matsubara [87] pioneered the transfer of the “bulky yet flexible” concept from palladium to nickel-based coupling reactions. The combination of nickel with other “bulky yet flexible” ligands such as CAACs [88,89] and abnormal NHCs [90] also saw some success. Moreover, Montgomery [91], Louie [92] and Johnson [93] used this concept to further investigate and consequently advance the synthesis and catalytic application of styrene-based nickel complexes, thus building upon the work of Belderrain and Nicasio [94].

Future advances, in particular through mechanistic studies, will provide insights into the exact role of electronic and steric parameters of NHC ligands on catalyst activity, thus guiding further catalyst design efforts across the periodic table. Nonetheless, these “bulky yet flexible” NHCs have already pushed the limits of highly hindered cross-coupling reactions, and hold great promise for combined high activity and catalyst recycling for numerous other metal systems.

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