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Review

Cross-coupling reactions catalysed by palladium pincer complexes. A review of recent advances

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Dedication: With great admiration for his enormous contributions to Organometallic Chemistry. Parabéns Armando!!!

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ABSTRACT

This paper provides a general overview of palladium pincer complexes, their structural diversity and synthetic protocols to further review the state of the art and recent advances on the organometallic chemistry of palladium pincer complexes bearing aryl and pyridine central backbones with special emphasis on their *DCD, PCP, NCN, SCS, OCO, SeCSe, DCD′and DND′* variants and their further applications on cross-coupling and related reactions, such as: Mizoroki-Heck, Suzuki-Miyaura, Sonogashira, Hiyama and Negishi couplings along with the allylation of aldehydes and arylation of azoles and indoles. A general discussion on the most active palladium pincer complexes in each process will also be provided.

Contents

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1. Introduction

In the last two decades, the chemistry of palladacycles has gained great relevance due in great part to their catalytic properties, being these compounds among the most active catalysts known for C–C and C–heteroatom bond formation. The simplest palladacycle contains at least one Pd-C bond in its structure. Pincer complexes are therefore a subclass of these species incorporating two fused palladacycles (Fig. 1) where the metallated carbon is supported by two donor groups in a κ^3-*mer* D-C-D fashion [1,2]. The donor groups (D) are typically neutral species, such as PR_2, $P(OR)_2$, NR_2, OR or SR, that along with their spacers are usually named "side arms", that stabilise the pincer complexes and strongly affect the electronics of the palladium center. Interestingly, in some cases, the replacement of carbon in the organometallic Pd–C bond with isoelectronic fragments containing silicon [3–6], phosphorous [7], boron anion [8] or neutral aromatic nitrogen atom [9–11] (B, Fig. 1) leads to important improvements in the catalytic activity. Another modification that enhances their activity is the use of two different donors (DCD'or DND′) on the side arms, leading to asymmetric palladium pincer complexes [12]. Analogously, tuning of the bulkiness of substituents in the side arms modifies the reactivity of the pincer complexes, since the meridional oriented pincer ligand is coplanar to the available coordination site. Thus, one of the most attractive features of pincer compounds and particularly of their palladium derivatives is the somewhat simple and facile tuning of both their sterics and electronics in order to improve their catalytic activity in a given way.

Historically, Palladium (II) pincer complexes have received a lot of attention due to their proper balance between stability and reactivity and because of their high catalytic activity in C-C bond forming reactions [2,13]. Additionally, most of these complexes are air and moisture stable, facilitating their handling and storage, resulting in long lasting lifetime catalysts and broad reaction scope.

The high stability, a consequence of the firm tridentate coordination of the ligands, is a key feature of pincer complexes and allows their use as catalysts at elevated temperatures. However, most of the current palladium-catalysed reactions are based on Pd(0)/Pd(II) catalytic cycles, which is easily susceptible to limitations of the deleterious β-hydride elimination from Pd(II), leading to a usually irreversible cleavage of the palladium-carbon bond and the decomposition of the complex. In fact, several research groups using palladacycles for C–C bond couplings, have reported, that often, nor the palladacycles nor the pincer palladium complexes are the true catalysts in these processes, but palladium nanoparticles or other weakly low-ligated palladium species. However, Milstein and co-workers proved that under mild reaction conditions the palladium (II) center in DCD ($D = PR_3$) pincer complexes may undergo reversible Pd(II) to Pd(IV) transformations regenerating the DCD system [14]. Compared with the Pd(0)/Pd(II) cycle, the Pd(II)/Pd(IV) cycle is more promising for the facile reductive elimination step from a Pd(IV) center and more chemoselective for the oxidative addition on Pd(II), but the oxidation of Pd(II) to Pd(IV) is a thermodynamically disfavoured process due to the electronic deficiency of the Pd(IV) center. In this context and considering the strong electron-donating character of pincer ligands, these seem like a suitable option to support and stabilise Pd(IV) complexes. To date, several reports on Pd(IV) pincer complexes as catalytic intermediates have been described, expanding the scope of palladium-based catalyst [15–18]. Thus, the present paper focuses on recent advances (last ten years) on palladium pincer complexes containing aryl and pyridine moieties as a central structural core unit (*i.e.* DCD or DND, respectively) and their use in organic synthesis in cross-coupling reactions.

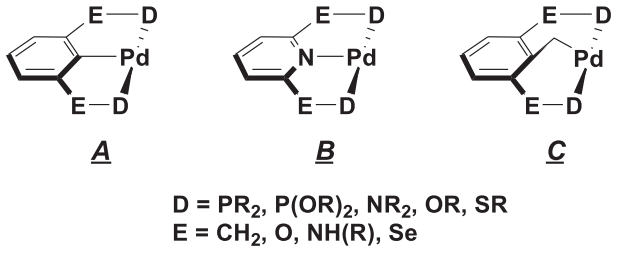


Fig. 1. General structures of palladium pincer complexes.

2. Well-defined palladium pincer complexes bearing aryl or pyridine backbones

Since the first pincer complexes were synthesized in the late 1970s a great interest in the development of novel pincer systems has emerged, associated with their ever-increasing applications in catalysis. Thus, in the last decade, a wide variety of pincer structures have been designed and synthesized with various transition metals as well as with different ancillary ligands [19,20]. Hence, nowadays the range of pincer metal complexes is extremely broad and keeps increasing continuously. In Fig. 2, a series of representative palladium pincer complexes are shown. These include aryl- or pyridine-supported complexes synthesized in the last years and used in cross-coupling and other related reactions.

Palladium complexes exhibit a plethora of diverse and excellent catalytic performances; thus, palladium catalysts have become one of the most important tools in organic synthesis, this being particularly true in cross-coupling reactions. Palladium-based pincer complexes with central aryl or pyridine donors, have been widely investigated and in the last ten years more than 100 palladium pincer complexes containing architectures of the type **A** and **B** (Fig. 1) have been described in the literature (Figs. 3–7) (only the general backbone was considered for this classification, chiral examples are not included).

3. Synthetic procedures

The use of a catalyst relays not only in its reactivity in a given process but also on how facile its attaining in high yields is. Thus, the procedure for the introduction of the metal on the pincer ligands is very important and to date, several methods have been developed to afford new pincer complexes in an efficient manner. The applicability of these methods strongly depends on the transition metal **M** and the donors D of the pincer ligand. Hence, this section describes the most representative methodologies employed for the synthesis of palladium pincer complexes including aryl (DCD) pincer backbones.

3.1. Pd-DCD pincer complexes

The synthesis of aryl-based pincer complexes is generally carried out by direct metallation *via* C-H bond activation [21–24], oxidative addition or transmetallation reactions (Scheme 1).

Among these procedures, the direct C-H bond activation is probably the simplest and major strategy used for the preparation of palladium pincer complexes because it does not require the prefunctionalization of the pincer ligands. Common palladium agents include palladium (II) salts such as $[Pd(OCOCF_3)_2]$ [25], $[Pd(BF_4)_2(CH_3CN)_4]$ [26–28], etc., Some of these reactions usually proceed in the presence of a base or by the use of $[Pd(CH_3COO)_2]$ using benzene, toluene or acetic acid as preferred solvents [29–31]. However, the success of this procedure is determined by the sterics

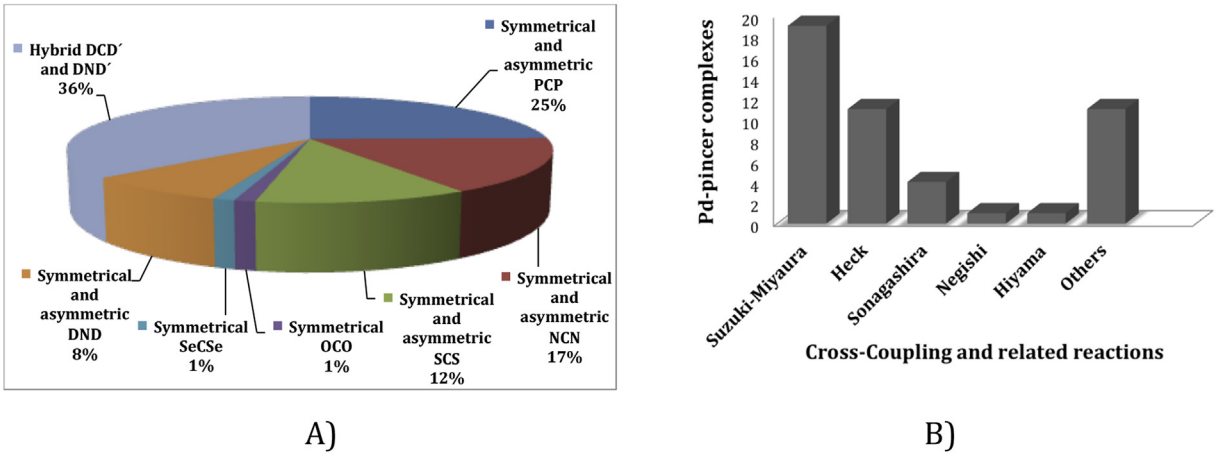


Fig. 2. a) Representative examples of different Pd-pincer complexes bearing aryl or pyridine backbones reported from 2005 to 2018; b) their applications in cross-coupling reactions (SciFinder®).

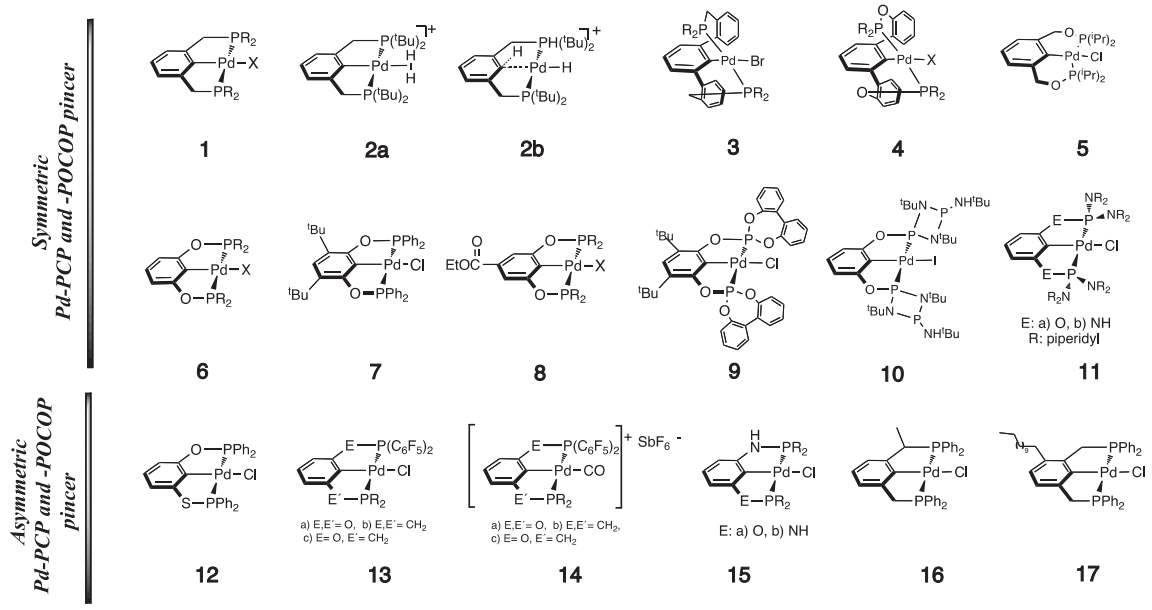


Fig. 3. Examples of symmetric and asymmetric Pd-PCP, Pd-POCOP pincer complexes.

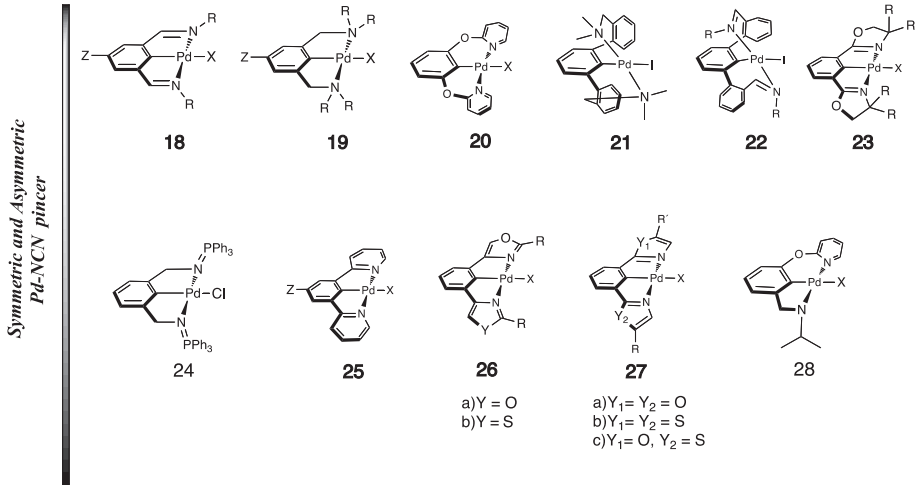


Fig. 4. Examples of symmetric and asymmetric Pd-NCN pincer complexes.

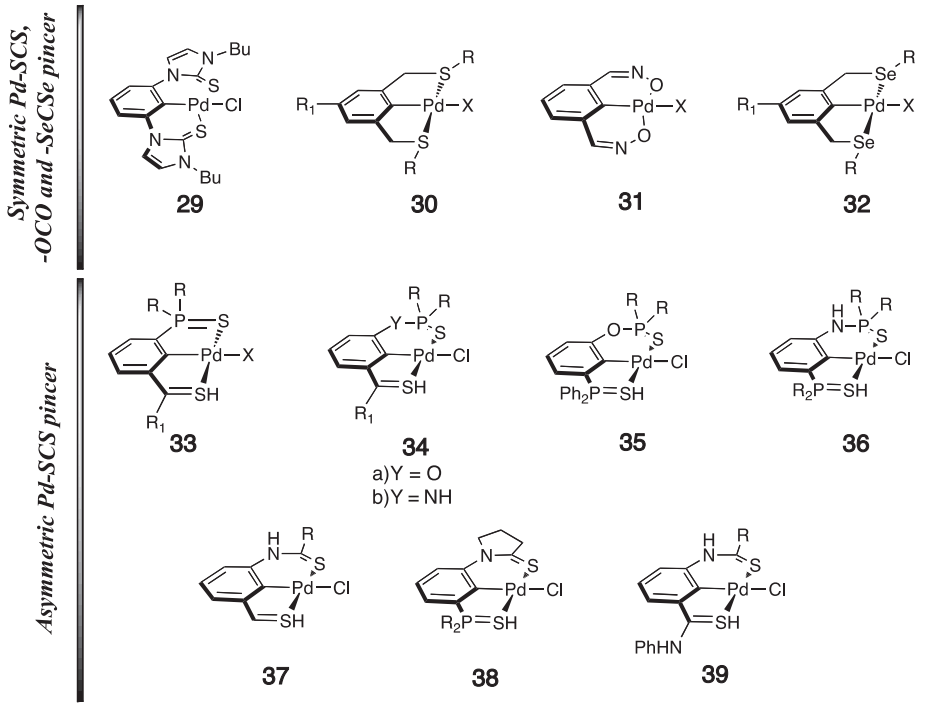


Fig. 5. Examples of symmetric Pd-SCS, Pd-OCO, Pd-SeCSe and asymmetric Pd-SCS pincer complexes.

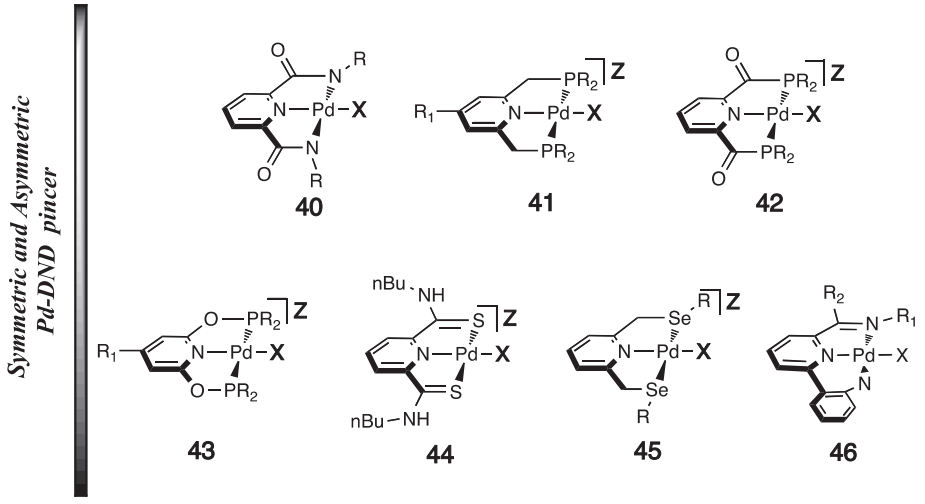


Fig. 6. Examples of symmetric and asymmetric Pd-DND pincer complexes.

and electronics of the side arms of the ligands. A drawback of the direct C-H bond activation process is that in many cases high temperatures and long reaction times are required driving the reaction to the formation of side products or decomposition.

On the other hand, oxidative addition is a very useful method to prepare palladium pincer complexes that cannot be synthesized by direct C-H bond activation procedures, naturally, this method is based on an oxidative addition process of Pd(0) species, generally $[Pd(dba)_3]$ or $[Pd(PPh_3)_4]$, among others, to a carbon-halogen bond of the pincer proligand [32,33]. This method is quite important for the generation of metal pincer complexes that contain various reactive groups in the same pincer architecture. However, a major drawback of this methodology is the accessibility to halide functionalized starting materials, which in many cases are hard to synthesize and often require tedious, low yield, multistep procedures to be prepared [34].

Another common method for the attaining of pincer complexes is the transmetallation process. This procedure uses either organolithium or organomercury as transmetalation reagents. For instance, lithiation of DCD ($D = PR_3$) ligands generally does not occur at the arene, but predominantly affords products lithiated at the benzylic positions of the DCD ligands. The use of an aryl halide starting material enhances the selectivity since Li/halide exchange is quantitative. However, the aryllithium species are generally not stable and isomerize to the benzyllithium complexes. This migration has been efficiently suppressed only when methyl groups are used as substituents ($D = PMe_2$). On the other hand, transmetallation reactions of DCD ($D = NR_2$) ligand precursors have been extensively applied to afford palladium pincer complexes of the NCN-*type* [35].

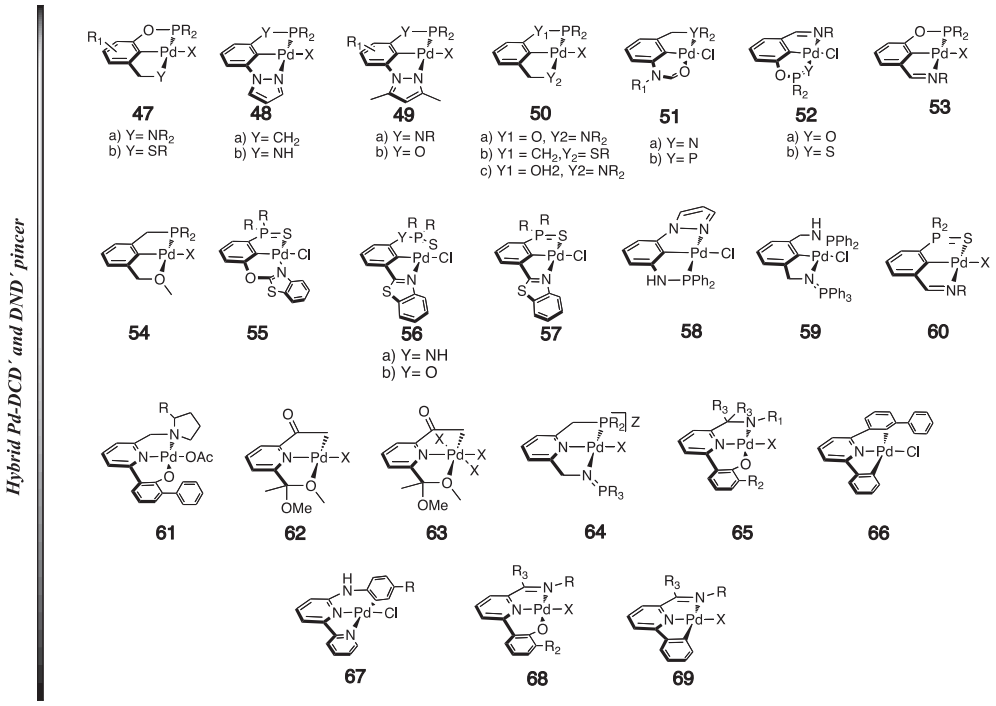
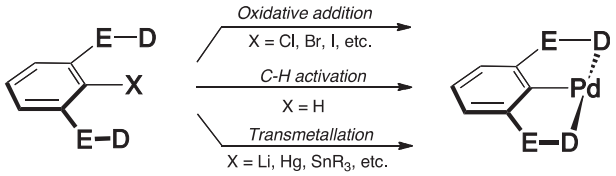
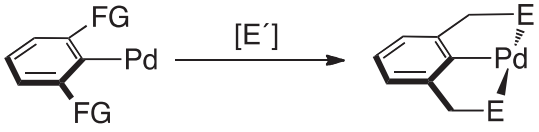


Fig. 7. Examples of hybrid Pd-DCD´and Pd-DND´pincer complexes.



Scheme 1. Synthetic protocols to generate palladium pincer complexes.



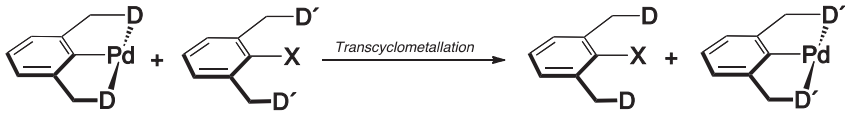
Scheme 3. Uozumi methodology: ligand introduction route.

More recently, other methods have been introduced for preparing metal pincer complexes such as the transcyclometallation reaction [36,37], in which the substitution of one cyclometallated ligand is carried out by another without the formation of significantly detectable amounts of purely organic compounds (Scheme 2) [38,39]. Remarkably, the transcyclometallation reaction has enabled the metallation of polyfunctional cartwheel ligands [40], which could not be cyclometallated by any of the three procedures described above. Thus, this method represents a different and, in certain cases, a superior methodology for metal insertion [40].

Finally, the ligand introduction route represents an interesting alternative methodology, this was first described by Uozumi and co-workers [41–44]. One of the most important advantages of this procedure is that it circumvents the problems caused by bulky substituents in the side arms. The basic element of this strategy is the introduction of the metal atom in an early stage of the synthesis of the complexes, and therefore, this method is called *ligand introduction route* (Scheme 3).

3.2. Pd-PCP pincer complexes

In general, symmetric PCP complexes are easier to synthesize compared with the asymmetric ones and thus, the former have been widely synthesized and studied (Fig. 3; 1 [45–47], 2 [48], 3 [49]). A remarkable example using a symmetric Pd-PCP to produce the first palladium dihydrogen complex (Fig. 3; 2a and 2b) was described by Heinekey et al. who showed the PCP ligand to be non-innocent in strong acid conditions observing sigma bonds (H-H and C-H) in the Pd-PCP complex that interact with the palladium center [48]. On the other hand, Pd-POCOP complexes are a subclass of the Pd-PCP family exhibiting similar characteristics of robustness and thermal stability that their phosphine congeners, and in many cases, the Pd-POCOP have demonstrated to be superior, exhibiting outstanding catalytic activities (Fig. 3; 4 [50], 5 [51], 6 [42,52–54], 7, 8 [55], 9 [56], 10 [57], 11a [58], 13a [59], 14a [59], 15a [60]). Additionally, the Pd-POCOP complexes can be easily synthesized in consecutive reactions from a resorcinol derivative, and the appropriate chlorophosphine in the presence of a palladium source and a



Scheme 2. Transcyclometallation reaction.

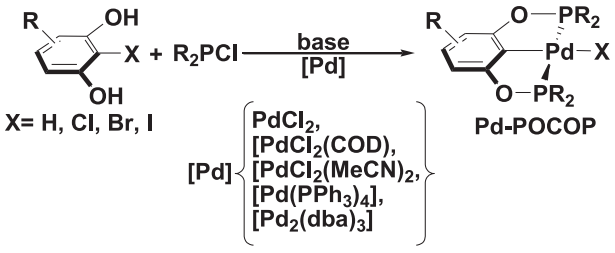
base. The facile preparation of these complexes is probably the greatest advantage over their phosphine analogues (Scheme 4).

The consideration of having different substituents in the pincer ligand and thus combine different donor and/or steric properties to induce the potential participation of the ligand in a given process, has led not just to the synthesis of different asymmetric pincer compounds but to the discovery of different and interesting transformations where the ligand tends to play an important role. Thus, during the past decade, the number of asymmetric pincer complexes has increased considerably. However, nowadays these complexes are still limited compared to the symmetric ones due in great part to the difficulties in their preparation, often being laborious, including multiple step synthetic procedures (Fig. 3; 12 [61], 13b and c [59], 14b and c [59], 15b [60], 16 [62], 17 [63]) often leading to low yields. Nevertheless, the complexes bearing asymmetric pincer ligands have shown, in many cases, enhanced reactivities that clearly justify their synthesis and worthy its further exploration.

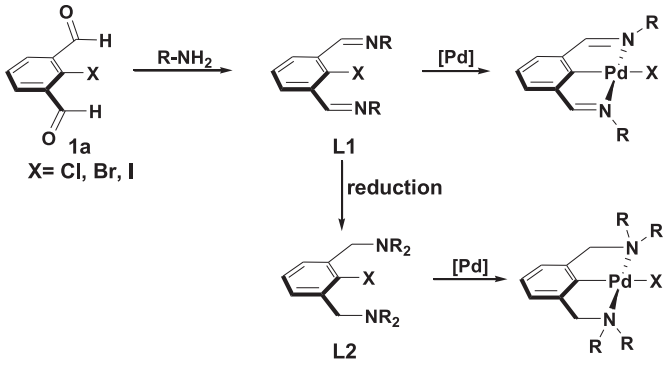
3.3. Pd-NCN pincer complexes

Although the Pd-PCP pincer complexes have received much attention, Pd-NCN pincer complexes have shown interesting properties that make them suitable for many transformations and catalytic experiments. In general, they tend to be more stable towards moisture and air that their Pd-PCP counterparts. Their synthesis is relatively simple, making easy the fine-tune of the NCN pincer platform by changing different functional groups within their multiple anchoring points (Fig. 4; 20 [64], 23 [65], 24 [66], 25 [67], 26 [68], 27 [69–71], 28 [72]). These efforts have led to the construction of chiral pincer scaffolds and complexes that offer promising utility in asymmetric catalytic synthesis. While the production of several M-PCP complexes can be achieved by reaction of metal salts with donor substituted hydrocarbons (C-H activation), it has been found that the synthesis of NCN pincer complexes often fails when using the corresponding NC(H)N ligand precursors [73,74] requiring more reactive N(C-X)N (X = Cl, Br, I) ligands (Fig. 4; 18 [41,75,76], 19 [77–81], 21 [82], 22 [83]). A general method to produce NCN pincer complexes is shown in Scheme 5, in which the condensation of **1a** with the appropriate amine affords the corresponding diimine ligand precursor L1, and ligand L2 can be obtained by the reduction of L1. Both ligands in the presence of $[Pd_2(dba)_3]$ produce the corresponding Pd-NCN pincer complexes (Fig. 4; 18, 19).

Another common problem in the synthesis of Pd-NCN complexes is that many imine ligands are chemically unstable and these are not suitable for metallation, and substantial decomposition of the ligands under common reaction conditions has been observed [84,85]. In this regard, the ligand introduction route has demonstrated to be efficient to produce Pd-NCN complexes containing imine moieties in high yields (Scheme 6).



Scheme 4. Synthesis of Pd-POCOP complexes.



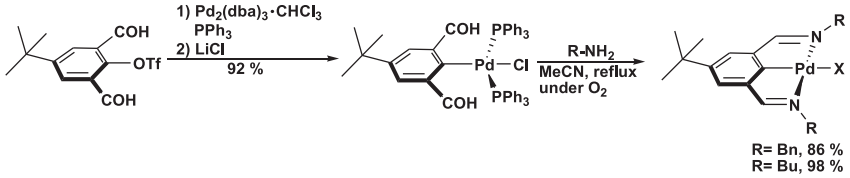
Scheme 5. General method to synthetize NCN-type pincer complexes.

3.4. Pd- SCS, -OCO, -SeCSe pincer complexes

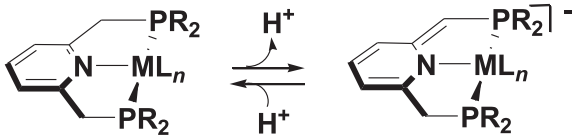
Another group of pincer compounds that have not been greatly explored include donor atoms from Group 16. Thus, since Shaw reported the first SCS pincer complex in 1980 [86], a thioether-based palladium derivative, a great variety of symmetric and asymmetric SCS pincer complexes have been synthesized exhibiting a rich architectural diversity including lateral donors such as thioethers (Fig. 5; 30 [87–90]), thioamides (Fig. 5; 29 [91], 37 [92], 38 [92], 39 [92]), or phosphine sulphides (Fig. 5; 33 [93], 34 [93], 35 [94], 36 [92]). Recently, Kozlov and co-workers have reported a novel and simple method to obtain Pd-SCS pincer complexes in solid phase by manual grinding, *via* direct cyclopalladation upon heating in high yields [95] (Fig. 5; 37, 38, 39). Although the chemistry of SCS pincer has not been well developed as that of the related PCP and NCN derivatives, they have exhibited interesting properties and various catalytic applications ranging from borylation of allylic alcohols [96] to a variety of cross-coupling reactions [26,89]. In 2004, the synthesis of the first Pd-SeCSe pincer complex was reported by Yao et al. [97] demonstrating that the Pd-SeCSe complexes are extremely active catalysts for the Mizoroki-Heck couplings. The catalytic activity of the selenide-based Pd(II)-SeCSe pincer complexes not only rivals but vastly outperforms that of the corresponding phosphorus and sulphur analogues. Practical advantages of the selenium-based catalysts include their straightforward synthesis and high activity in the absence of any additives as well as the enhanced stability of the selenide ligands towards air oxidation (Fig. 5; 32 [98,99]). On the other hand, reports on OCO-pincer systems are rather limited [100,101] probably due to the weak donating capacity of neutral oxygen atoms or reactivity of the anionic oxygen atoms such that these systems failed to behave as spectator ligands. In this context, Li and co-workers designed a nitrone-based OCO-type ligand in which the dipolar nature of the nitrone renders the O atom a stronger donor, affording the Pd-OCO complex 32 [102] (Fig. 5). This Pd-OCO pincer complex has shown high activity in Mizoroki-Heck and Kumada cross-coupling reactions.

Pyridine-based pincer complexes are of particular importance because of their diverse chemistry, that includes aptitude for both catalysis and luminescence. One of the most important features of these ligands is that the rigid tridentate backbone allows de-aromatisation of the central pyridine ring induced by deprotonation of the methylene moiety on the PNP pincer ligand [103,104] (Scheme 7).

The facile de-aromatisation of the pyridine ring by deprotonation introduces metal-ligand cooperativity, which is less likely in the PCP analogues due to the high de-aromatisation energy. This non-innocent behaviour and charge switching character of the



Scheme 6. Synthesis of Pd-NCN pincer complexes employing the ligand introduction route.



Scheme 7. General representation of de-aromatisation of the pyridine ring by deprotonation on a PNP pincer complex.

pyridine based DND pincer ligands play an essential role in a number of catalytic transformations such as hydrogenation of esters, amides and CO_2 [105,106], dehydrogenative coupling and other related reactions [107,108]. Symmetric and asymmetric examples of Pd-DND pincer systems have been reported in the last decade and are shown in Fig. 6 (40 [109,110], 41 [111–113], 42 [114], 43 [115], 44 [116,117], 45 [118], 46 [119]).

3.5. Asymmetric Pd-DCD′and Pd-DND′ pincer complexes

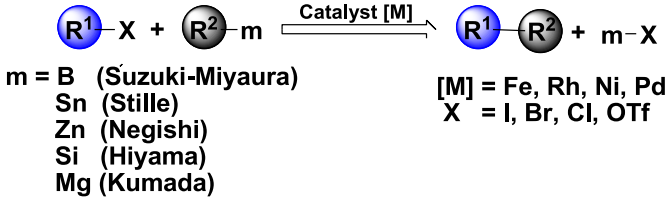
The variety of available pincer ligands has increased in recent years. While early pincer ligands were symmetric, with respect to ligand "arms", pincer-type complexes bearing asymmetric arms have begun to appear in greater number (Fig. 7). The hybrid asymmetric DCD'and DND′-pincer palladium systems having two different donor arms, typically one soft P-donor and one hard donor N- or O-donor (47a [120–123], 48b [124,125], 49,[126, 127] 50a and c [26,128,129], 51b [130,131], 53 [132], 54 [133], 58 [134], 59, 64 [135]) have received particular attention, as such systems render complementary properties of both the soft/hard donors as well as that of the distinct electron-donor/acceptor ability. The inclusion of a donor moiety on one arm of the pincer that does not bind tightly to the metal provides potential access to an available site in the coordination sphere. This hemilabile attribute of the ligand allows the ligand to coordinate in a tridentate configuration in some situations and in a bidentate manner in others. Scheme 8 depicts an example of a hemilabile Pd-PCO pincer complex (Fig. 7; 54 [133]) in which the ligand is coordinated in three different fashions to the palladium center under diverse reaction conditions. These three species were isolated and characterised by single-crystal X-ray crystallography.

The presence of a hemilabile ligand in a complex may lead to a dramatic rate enhancement in catalytic reactions or significantly influence the reactivity of incoming substrates to promote transformations that would not otherwise occur [136]. In homogeneous catalysis, the hemilability phenomenon will provide a vacant coordination site at the metal center, leading to coordination, activation and transformation of the substrate molecules and stabilising the reactive intermediates. The importance of hemilability was first demonstrated in homogeneous catalysis where it continues to provide new and exciting results such activation of strong bonds and small molecules (H_2, CO, CO_2, H_2O) [133]. More recently ligand hemilability has also been applied to the development of new molecular-based sensors and materials [136]. Other interesting examples of hybrid systems Pd-PCS, - NCO, -NCS, -NCO, -NNO, -CNO, -NNC are presented in Fig. 7 (47b, 48a, 50b, 51a, 52 [137], 55 [138], 56 [95,138], 57 [138], 60 [139], 61 [140], 62 [141,142], 63 [142], 65 [143], 66 [144], 67 [145],68 [146], 69 [147]).

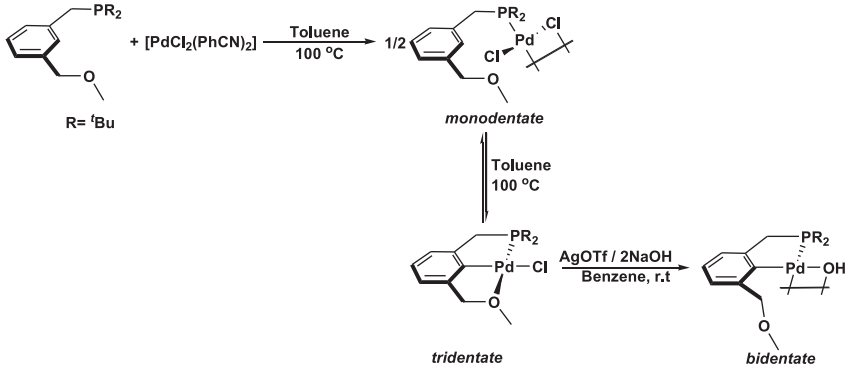
4. Cross-coupling reactions

Cross-coupling reactions represent one of the most important class of catalytic carbon-carbon bond forming reactions [148]. These processes consist of the carbon-carbon bond formation between an organic electrophile, R [1]-X, and an organometallic nucleophile, R^2-m, in the presence of a catalyst (Scheme 9).

The most widely used catalysts are based on transition metal



Scheme 9. General scheme of C-C cross-coupling reactions.



Scheme 8. Representative example of a hemilabile PCO pincer ligand.

complexes from Groups 8–10, and especially those of palladium. Likewise, pincer complex based catalysts have been extensively used in these processes. The first Mizoroki-Heck reaction with a palladium-pincer complex catalyst was reported by Milstein and co-workers [16], since then, a great number of publications have appeared on cross-coupling reactions using these compounds. The largest number of publications being on Suzuki-Miyaura [50,63,69,124,132,138,149–158] couplings and Heck-coupling/Heck-type reactions [18,51,63,64,89,140,159,160]. In addition, there are several recent publications on Sonogashira [124], Negishi [116], Stille [161,162], and Hiyama [124] couplings as well. On this regard, it is generally accepted that cross-coupling reactions follow a catalytic cycle consisting of three main steps: oxidative addition, transmetallation, and reductive elimination. However, to date, several studies concluded that the pincer complexes decompose under the applied, often harsh conditions, and the catalytic activity arise from Pd(0) decomposition products [1,28,163]. Nevertheless, a great number of studies have presented convincing evidence that palladium pincer complexes are the direct catalysts in coupling reactions. In these studies, one of the most questionable issues in the mechanism is the redox process of the palladium atom to Pd(0) which leads to cleavage of the palladium-carbon bond and usually decomposition of the complex. On the other hand, oxidation to Pd(IV) is a thermodynamically disfavoured process requiring strong oxidants. Despite the wide use of cross-coupling reactions, their application has been often based on a trial-and-error approach, because mechanistic knowledge has been difficult to acquire just with experimental techniques. In this regard, several DFT modelling studies have been published on this topic [18,164].

4.1. Mizoroki-Heck couplings

Heck coupling reaction is among the most important transformation based on Pd catalysts. Much effort has been devoted to the expansion of the scope of this C-C bond forming reaction by means of several catalytic systems. A conventional Heck coupling is based on an iodide, bromide or chloride derivative R-X and a α-olefin. The most efficient C-C bond formations arise when the olefin possesses an electron-withdrawing group. Most frequently, the Heck reaction is catalysed by Pd(II) or Pd(O) derivatives in the presence of an auxiliary ligand, generally, in excess. Unfortunately, the reaction intermediates formed during the catalytic reaction are sensitive to oxygen or thermally unstable. Thus, with the aim to find more stable, robust and efficient catalysts, Milstein et al. [16] tested the first palladium pincer complexes (Pd-PCP) in the heck reaction, finding these compounds to be active catalysts with turnovers numbers of 500000 in the couplings of iodobenzene with methylacrylate without noticeable catalyst degradation. The high stability of pincer complexes under harsh conditions and the achievement of high TON's strongly stimulated the development of pincer complex catalysed reactions. In this context, Morales-Morales & Jensen [17] reported a Pd-POCOP pincer complex phosphinite-based reaction, which was found efficient in the coupling of the industrially important aryl chlorides with good yields and showed to be as reactive as the Pd-PCP phosphine derivative described previously by Milstein (Fig. 8).

In 2007, Morales-Morales, Jensen and co-workers [51] synthesized the first example of a six-membered PCP pincer bis(phosphinite) (5), which was found to be catalytically more efficient than their five-membered counterparts previously reported by Milstein and Morales-Morales, even for the coupling of deactivated and sterically hindered aryl chlorides with high turnover numbers (Table 1). The high activity showed by complex 5 was rationalised in terms of the length of the pincer arms and the size of the palladacycle that could cause an increase in the P-M-P bite angle and, therefore, to provide a more flexible system.

In 2009, Sing et al. [118] reported the synthesis and catalytic activity of the complex Pd-SeNSe (45) in coupling reactions of bromobenzene and iodobenzene derivatives with styrene/*n*-butyl acrylate exhibiting high yields and turnover numbers of 6500 and 95000 respectively (Fig. 9). Another remarkable example was informed by Ahn et al. [64], who synthesized a six-membered fused metallacycle complex of the type Pd-NCN (20). Complex 20 showed exceedingly high turnover numbers in the coupling reactions of iodobenzene and bromobenzene with methyl acrylate with turnover numbers up to 8.4×10^8 (Fig. 9).

Finally, the Pd-NCP (58) complex was also examined in Heck reactions using DMF and water as solvents exhibiting high activities in both cases (Scheme 10) [134] and showing the performance of the catalyst to be strongly dependant of the solvent.

4.2. Suzuki-Miyaura couplings

The Suzuki-Miyaura reaction is one of the most versatile synthetic and successful methods for the construction of biaryls and substituted aromatic moieties. This reaction takes place between an organic halide (or triflate), R [1]-X and a boronic acid R [2]-B(OH)$_2$, in the presence of a base. As it could be expected organopalladium compounds, and thus Pd(II)-pincer complexes have also been successfully applied as catalysts for this reaction. Some representative examples include aryl-based PCP (4 [50], 6 [42], 11 [150], 17 [63]), NCN (27 [69,71]), SCS (29 [91], 30 [87], 33 [93], 34 [93], 35 [94]), hybrid DCD' (48 [124], 49 [126], 52 [137], 53 [132], 55 [138], 56 [138], 57 [138], 60 [139]), as well as pyridine-based DND′(61 [140], 69 [147]) type pincer complexes that have been successfully employed in Suzuki-Miyaura coupling reactions. Selected catalytic results obtained by using some of these Pd pincer complexes are shown in Table 2 and Fig. 10.

Among them, the activity of the PCP complex (11b) was rather impressive, ranking as one the best pincer complexes suggested for this reaction. Both aryl bromides and more challenging chlorides could be converted to the coupled products in short times with low catalyst loadings (Table 2, entries 2 and 3). This reaction was characterised by a negative mercury drop test, and the complex 11b could be completely recovered after the reaction proceeds, thus proving the pincer compound to be the true catalyst. According to the authors, these findings indicate that Pd(0) species/nanoparticles cannot be the active catalyst, which led to the conclusion

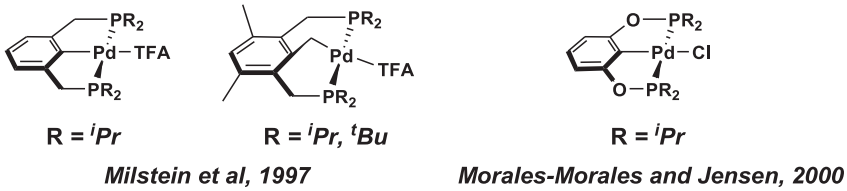
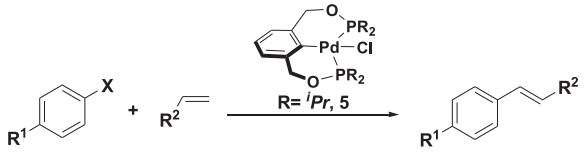
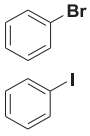


Fig. 8. Examples of palladium pincer complex tested in *Mizoroki-Heck coupling reactions*. More recently, other Pd-pincer complexes have been reported as efficient catalysts in the Heck reaction including PCP (1 [47], 5 [51], 17 [63]), NCN (18 [41], 20 [64], 26 [68]), SCS (29 [91]), SeNSe (45 [118]) and the hybrid asymmetric NCP (58 [134]) and ONN (61 [140]).

Table 1
Heck-Mizoroki couplings catalysed by complex 5.



Entry	[Pd] (mol %)	Aryl-halide	Olefin R^2	Reaction Conditions	Yield (%)	TON
1	5 (0.**01**)		Ph	N_2CO_3, NMP, 180 °C	94	9400
2	5 (0.**006**)		*n*-butyl methacrylate	N_2CO_3, NMP, 180 °C	100	16667
3	5 (0.**01**)		*n*-butyl methacrylate	N_2CO_3, NMP, 180 °C	99	16667

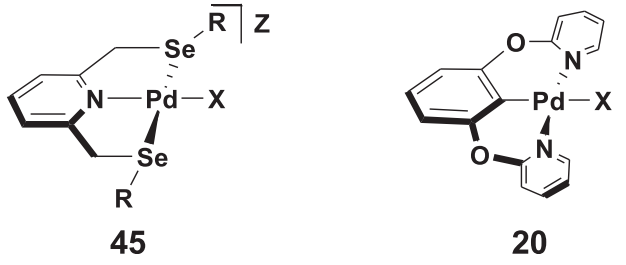
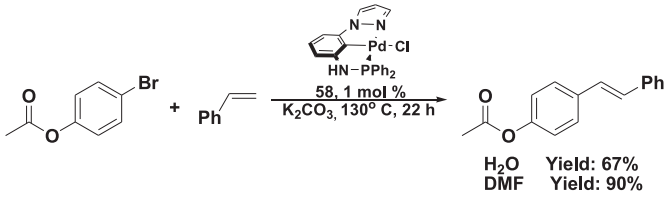


Fig. 9. Remarkable examples of palladium pincer complex tested in *Mizoroki-Heck coupling reactions.*



Scheme 10. Heck reaction catalysed by the Pd-NCP pincer complex, 58.

that a cross-coupling reaction occurs via a Pd(II)/Pd(IV) catalytic cycle [150].

The hybrid PCN complex (48b[124]) was also a very efficient catalyst exhibiting high activity and more important, using mild reaction conditions and water as solvent (Table 2, Entry 6). The hybrid SCN complex (57) also showed good catalytic activity with aryl bromides (Table 2, Entry 8) and aryl chlorides (49%). It is noteworthy that hybrid complexes Pd-PCN (48) and Pd-ONN (61[140]) are the most versatile pincer catalyst. The Pd-PCN complex (48) also catalyses the Sonogashira and Hiyama couplings and the Pd-ONN complex (61) is active in hydrogenation and the hydrosilylation processes.

4.3. Sonogashira couplings

The Sonogashira coupling is a widely used method for the preparation of arylalkynes and conjugated enynes. The general protocol for the reaction of terminal alkynes with aryl or alkenyl halides usually involves a Pd(0)/Cu(I) catalytic system and at least stoichiometric amounts of a base. The presence of a Cu(I) salt is generally believed to facilitate the transfer of the alkynyl group to

Table 2
Suzuki-Miyaura coupling catalysed by complex 11b.

Entry	[Pd] (mol %)	Aryl-halide	Arylboronic acid	Reaction conditions	Yield (%)
1	6 (0.**01**)			K_2CO_3, toluene, 130 °C, 24 h	58
2	11b (**0.001**)			K_3PO_4, toluene, 100 °C, 5 min.	95
3	11b (**0.1**)			K_3PO_4, toluene, 100 °C, 1.5 h	99
4	27a (**0.0001**)			K_3PO_4, dioxane, 100 °C, 16 h	79
5	34a (**0.01**)			K_3PO_4, Bu_4NBr, DMF, 120 °C, 5 h	100
6	48b (**0.1**)			K_3PO_4, H_2O, 50 °C, 2 h	80
7	52b (**0.01**)			K_3PO_4, Bu_4NBr, DMF, 120 °C, 5 h	100
8	57 (**0.01**)			K_3PO_4, DMF, 120 °C, 5 h	100
9	69 (**0.01**)			Cs_2CO_3, dioxane, 100 °C, 4 h	100

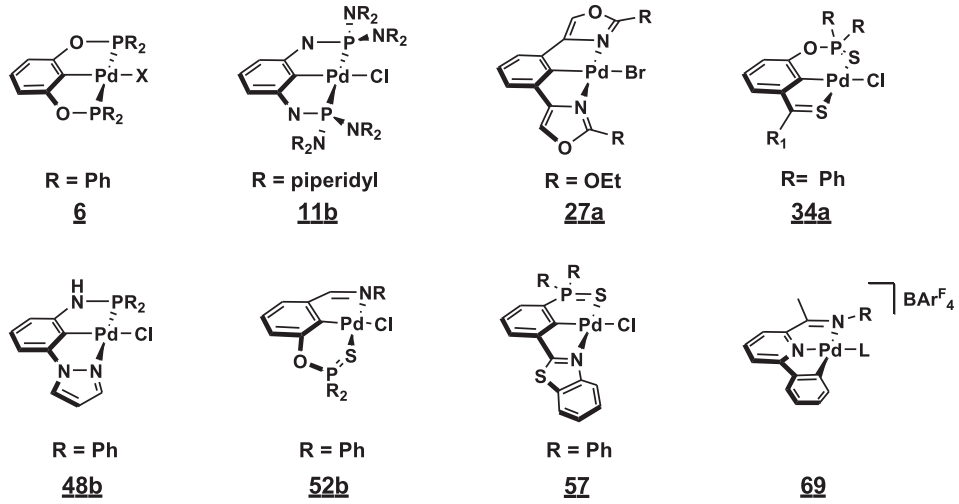


Fig. 10. Selected examples of palladium pincer complexes used as catalysts in *Suzuki-Miyaura coupling reactions.*

the Pd catalysts by *in situ* generation of copper acetylide species and the subsequent transmetallation of this group to Pd [165]. Because of its synthetic importance, several studies have been reported on the improvement of this process by using palladium pincer complexes; representative examples include PCP (11 [58]), SCS (29 [91]), NCN (18 [75]) and NCP (58 [124,134]), Figs. 10 and 11. For instance, French and co-workers [58] employed aminophosphine based complexes, such as 11b, as very efficient catalysts in Sonogashira couplings. The reaction proceeds in the absence of a copper co-catalyst with a TON of 2×10^6 in quantitative yields. Very recently, Wang et al. [75] reported the imine-based pincer catalyst 18, to be suitable to perform Sonogashira couplings. Here, the catalytic activity is dependent on the donor character of the substituent Z in the pincer, the highest activity being observed when $Z = NO_2$. Complexes 29 and 58 also showed to be active catalysts in Sonogashira reactions as well as in Suzuki-Miyaura and Mizoroki-Heck couplings. Complex 58 was found to be active in the coupling of iodobenzene with phenylacetylene, in the absence of copper, under mild conditions (50 °C, 24 h) using water as solvent, affording a 97% yield of the corresponding product. Furthermore, complex 58 was proved to be also a good catalyst in Hiyama reactions.

4.4. Hiyama and Negishi couplings

In addition to Suzuki-Miyaura, Mizoroki-Heck and Sonogashira couplings, Pd-pincer complexes have also been successfully used as efficient catalysts in other organic chemistry relevant cross-coupling reactions such as the Hiyama and Negishi reactions. Thus, in 2008, Arriortua et al. [124] reported the first Hiyama coupling reactions using an asymmetric Pd-NCP pincer complex (58) as catalyst, (Scheme 11). The coupling reaction of the corresponding silane and bromobenzene was carried out in water in the presence of NaOH as an activator, affording good yields of the corresponding coupling product.

On the other hand, the Negishi coupling of aryl iodides with alkyl zinc derivatives catalysed by the pincer complex Pd-SNS (44) was reported by Lei and co-workers [117] (Scheme 12). This reaction was performed under mild conditions affording the coupling product with a high selectivity along with the corresponding dehalogenated product. The reaction required very low catalyst loadings (0.00001 mol %) and proved to be easily scalable without a noticeable decrease of the yields, thus highlighting its potential industrial applications. Mechanistic studies of the Negishi reaction were also presented and according to these results it was established that the Pd-SNS (44) pincer complex is the true catalyst surviving the reaction conditions without any apparent decomposition.

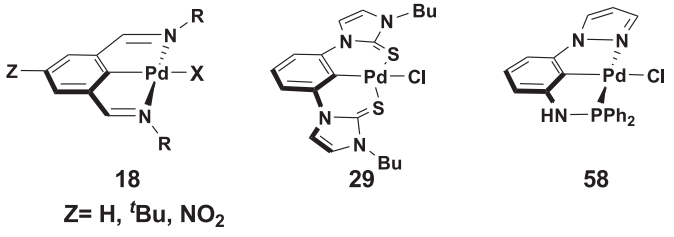
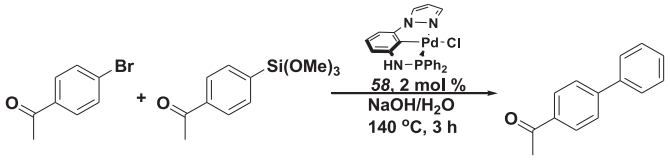


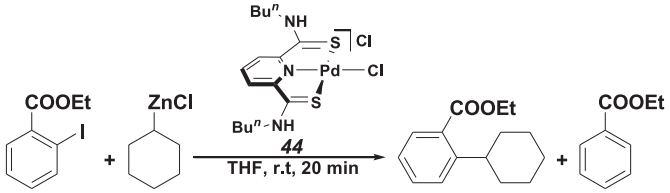
Fig. 11. Selected examples of palladium pincer complexes used as catalysts in *Sonogashira coupling reactions.*

4.5. Allylation of aldehydes

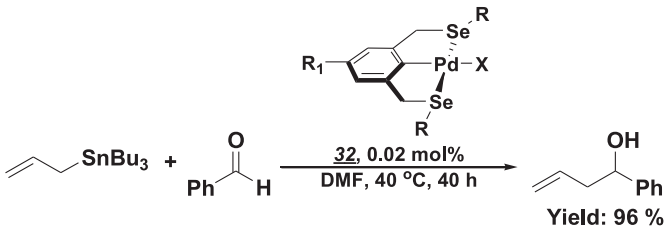
In addition to the most commonly known cross-coupling reactions, a variety of well-defined Pd-pincer complexes have also



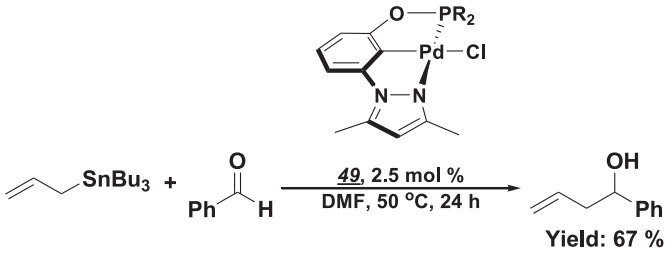
Scheme 11. Example of a Hiyama coupling reaction catalysed by an asymmetric Pd-NCP pincer complex, 58.



Scheme 12. Example of a Negishi coupling reaction catalysed by the Pd-SNS pincer complex, 44.



Scheme 13. Reaction of allylation of benzaldehyde allyltributyltin catalysed by Pd-SeCSe pincer complex, 32.



Scheme 14. Reaction of allylation of benzaldehyde allyltributyltin catalysed by Pd-PCN pincer complex, 49.

been employed to promote the allylation of aldehydes. The electrophilic allylation was pioneered by Yamamoto and co-workers [166–168]. The Szabó group [32,33] and others [22,98] have also demonstrated that palladium pincer complexes efficiently catalyse the electrophilic allylation of aldehydes and imines using stannanes or potassium trifluoro(allyl)borates [33,169]. The applications of palladium pincer catalysts in allylation reactions has a number of benefits compared to bis-allyl palladium chemistry. In 2003, Szabó and co-workers [170] reported the first PCP-type palladium pincer complex-catalysed electrophilic allylation of aldehydes proving to be successful for the coupling of allylic stannanes with aldehydes, obtaining the corresponding homoallylic alcohol in high yields and selectivity. Yao and co-workers [98] used the palladium pincer SeCSe complex (32) and found the allylation of benzaldehyde allyltributyltin to proceed with low catalyst loadings, affording the homoallylic alcohol in excellent yields (96%) under mild reaction conditions (Scheme 13). The same catalyst 32 was also found to be very active in the aldol type cyclization of isocyanoacetates and sulfonylimines, thus probing Pd-SeCSe pincer complexes as privileged catalysts for these processes.

In 2011, Song et al. [127] prepared the asymmetric Pd-PCN pincer compound (49) and applied it in the allylation of aldehydes. Unfortunately, this complex exhibited rather low activity in the allylation of benzaldehyde (Scheme 14). The same research group synthesized a hybrid Pd-CNN pincer complex and found it to be an efficient catalyst for the allylation of aldehydes as well as for the three component allylation of aldehydes, arylamines and allyltributyltin, being this the first time, this procedure was catalysed by a Pd-CNN complex [72].

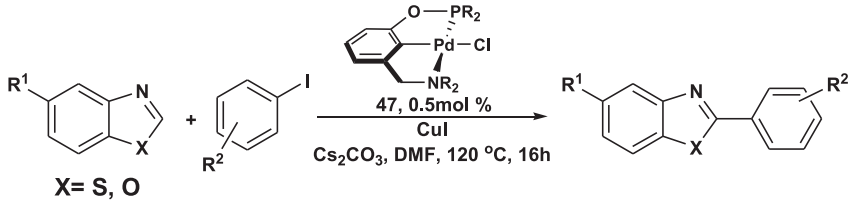
4.6. Arylation of azoles and indoles

Finally, very recently Punji and coworkers [120,122], inspired by the aminophosphine palladium pincer complex (11), designed and prepared a hybrid Pd-POCN pincer complex (47) envisioning an amino-phosphinite ligand where the electron-rich and hard donor amino side along with the phosphinite segment would assist in the electrophilic addition and transmetallation, respectively, thus, making this complex an ideal system to stabilise the catalytically active palladium species in higher oxidation states. Indeed, this compound catalyses the C-H bond arylation of azoles, being the first Pd-pincer catalyst used in this reaction that works efficiently in the coupling of a range of activated, deactivated and functionalized azoles with diverse aryl iodides using a low catalyst loading attaining TONs up to 650 (Scheme 15).

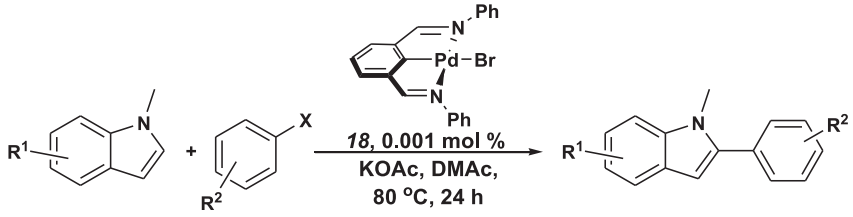
Moreover, in 2014 Cai and co-workers [76] reported the first selective C-2 arylation of N-methyl indoles, efficiently catalysed by a Pd-NCN pincer complex (18). The reaction was conducted under relatively mild conditions affording good yields (90%) and excellent selectivities with aryl iodides and moderate activities with aryl bromides (Scheme 16).

5. Conclusions and outlook

The chemistry of pincer compounds has evolved hand to hand with cross-coupling reactions and, in many occasions, it has been the actual motivation for the development of new pincer scaffolds, thus enriching the structural diversity of these species and their potential applications. The recent discoveries of the non-innocence of the pincer ligands and their symbiotic participation in different transformations have allowed the development of more efficient



Scheme 15. Arylation of azoles catalysed by the Pd-POCN complex, 47.



Scheme 16. Arylation of N-methyl indoles catalysed by the Pd-NCN pincer complex, 18.

pincer based catalysts advancing our knowledge and diversifying our vision on cross coupling-reactions. These advances in turn have let us to progressively use less reactive and cheaper starting materials, increasing the potential use of pincer species in the scaling up chemical transformations. Thus, the future developments of the chemistry of pincer compounds in organic synthesis look bright and promising, this being particularly true for cross-coupling reactions and other multiple applications yet to be discovered, this time catalysed by pincer compounds based on more earth abundant/cheap/biocompatible metals and learning from previous lessons [40] trying to properly functionalize [171] or support them and thus recover these catalysts in an attempt to closer to sustainable processes friendly with the environment.

Acknowledgments

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