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Review

Catalytic C–C coupling through C–H arylation of arenes or heteroarenes

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Dedicated to Fausto Calderazzo, a scientist of exceptional level and an old good friend.

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ABSTRACT

The present review refers to catalytic methods to arylate arene or heteroarene compounds. The resulting compounds are ubiquitous in biology and in pharmaceuticals or fine chemicals production. Until a few decades ago they were prepared according to laborious procedures often involving a series of steps all requiring product isolation. Catalytic methods are much simpler and convenient and often consist of one-pot procedures leading to highly selective reactions. The reaction types described here encompass intermolecular as well as intramolecular reactions. Assistance by chelating groups, heteroatoms and metallacycles are considered for metal-catalyzed reactions not involving the use of oxygen or stoichiometric oxidants.

1. Introduction

Catalytic formation of biaryl compounds has been the object of a variety of methods which successfully compete with the more laborious conventional ones. It is essentially based on the replacement of an aryl-bonded leaving group such as a halide with a suitable nucleophile under the catalytic action of a transition metal. The latter must be able to undergo oxidative addition of the aryl halide to afford an arylmetal halide (or other leaving group) complex, where substitution with an aryl group can take place. This latter group generally is another organometallic species such as Grignard, Stille and Negishi reagents or an arylboronic acid [1–4].

Direct C–H arylation of arene compounds overcomes the need for a functional group in one of the aryl moieties undergoing C–C coupling [5]. As we shall see, however, to obtain a selective reaction some type of assistance is usually necessary. For recent reviews on aryl–aryl coupling by metal catalyzed direct arylation see Refs. [6–12]. For the use of oxygen or stoichiometric oxidants, which are not considered here, see Ref. [13,14].

We shall deal with catalytic non-oxidative: (i) intermolecular C–H arylation of unactivated arenes; (ii) intramolecular arylation; (iii) assisted intermolecular arene C–H activation.

2. Intermolecular C–H arylation of unactivated arenes

Unactivated arenes such as benzene react efficiently with aryl iodides [15], in general according to an arene electrophilic substitution operated by an arylmetal complex formed by oxidative addition of an aryl halide to a low valent metal. Using

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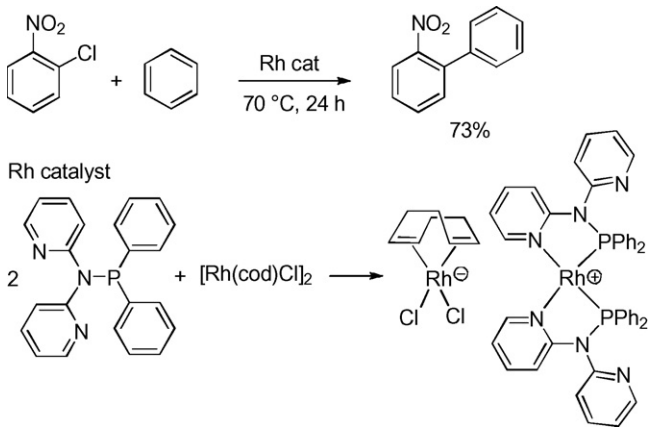


Scheme 1.

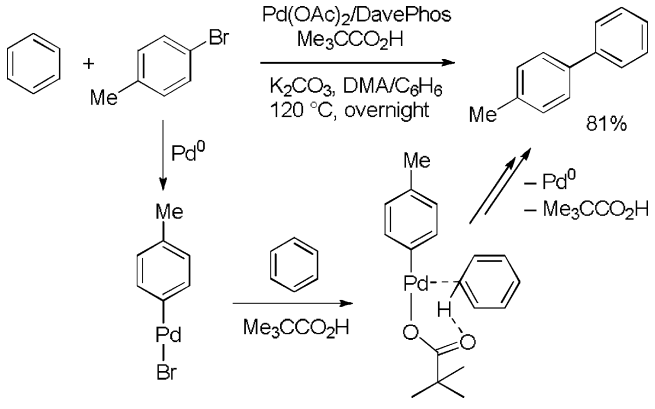
$[C_p^*Ir(H)Cl]_2$ ($C_p^* = C_5Me_5$) in the presence of *t*-BuOK as a base at 80 °C the cross-coupling reaction of 4-iodoanisole and benzene led to a 66% yield of 4-methoxybiphenyl. A new bimetallic Rh catalyst which tolerates functional groups was used to couple aryl bromides and chlorides with benzene at 70 °C with satisfactory yields and high turnover numbers. As shown in Scheme 1 the catalyst is formed in situ by reaction of [bis(2-pyridyl)amino]diphenylphosphine with half an equivalent of $[Rh(cod)Cl]_2$ (cod = cyclooctadiene). Both the anionic and cationic Rh species are needed for catalysis [16].

Radical mechanisms have been proposed both for Ir- [15] and Rh- [16] catalyzed reactions.

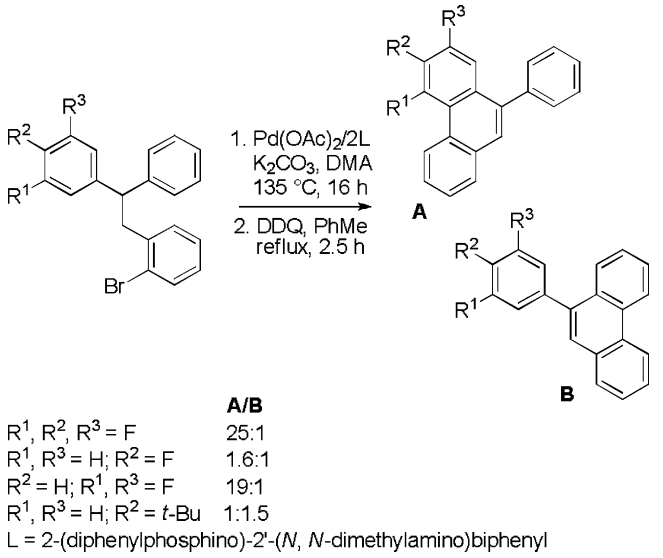
Pd catalysis has been successfully used to arylate the polar hydrocarbon azulene regioselectively at the electron-rich 1-position [17].

A recent achievement consists of the use of pivalic acid in the reaction of Pd(0) (from $Pd(OAc)_2$) with bromoarenes and benzene in the presence of K_2CO_3 at 120 °C (Scheme 2). 2-Dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl (DavePhos) was the ligand of choice for Pd [18]. The addition of 30 mol.% Me_3CCO_2H led to 4-methylbiphenyl in 81% yield from *p*-bromotoluene and benzene.

An intermediate in which the pivalate anion helps to abstract hydrogen from benzene has been postulated as first proposed by Echavarren [19]. Theoretical studies on aryl–aryl intramolecular coupling have shown that in many cases of intramolecular arene arylation substituent effect and kinetic isotopic effect are not compatible with the traditional electrophilic substitution mechanism and are best interpreted by a mechanism involving hydrogen abstraction by a base or by an appropriate ligand [19,20]. Experiments and theoretical calculations by Fagnou and coworkers have lent support to this interpretation [21], which appears to be valid for any type of intra and intermolecular arylation of arenes.



Scheme 2.



	A/B
R^1, R^2, R^3 = F	25:1
R^1, R^3 = H; R^2 = F	1.6:1
R^2 = H; R^1, R^3 = F	19:1
R^1, R^3 = H; R^2 = *t*-Bu	1:1.5

L = 2-(diphenylphosphino)-2'-(*N*, *N*-dimethylamino)biphenyl

Scheme 3.

Selectivity in the arene position to be arylated is a problem in these reactions and orienting groups such as the chelating ones (Section 4.1) or heteroatoms (Section 4.2) or bridges between the aryl coupling moieties [22a] can help to obtain acceptable results. Using *o*-bromobenzyldiarylmethane systems where one ring contained substituents while the other was unsubstituted, arylation occurred preferentially on the ring bearing electron-withdrawing substituents, including those like the methoxy one that behave electronegatively by inductive effect. Electron-releasing substituents such as the trimetylsilyl and the *tert*-butyl drove the reaction towards the unsubstituted ring. Selectivity depends on substituent position, the *ortho* position close to the C–H bond being the most sensitive (Scheme 3) [19b].

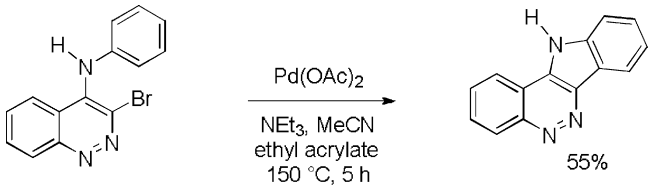
Pentafluorobenzene and other electron-poor perfluoroaromatics can be cross-coupled with aryl halides using as catalyst precursor $Pd(OAc)_2$ and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos) in isopropyl acetate [22b]. As in the pivalate case a base assisted C–H substitution mechanism has been postulated [22c]. According to theoretical calculations this mechanism also accounts for reactions of electron-rich arenes. DFT calculations by Fagnou's group have in fact confirmed the metalation–deprotonation mechanism and have led to predict the site of attack in a number of arylations, especially heteroatom assisted arylations. The similar outcome for very different structures has been explained as resulting from the balance between the expense of energy required for bringing the arene and the catalyst to the transition state (distortion energy) and the gain in electronic interaction energy due to bringing the two partners together [21].

The reader will be referred to the mechanistic results of these studies throughout the present review because of their general significance.

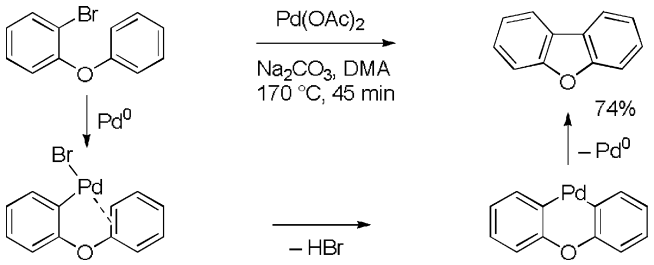
C–H arylation of arenes substituted by electron-withdrawing groups, has also been obtained extending the Cu-phenanthroline-based method cited in Section 4.2.

3. Intramolecular arene C–H arylation

In contrast with the intermolecular arene C–H arylation seen above the intramolecular arylation readily occurs selectively. The field is dominated by Pd catalysis.



Scheme 4.



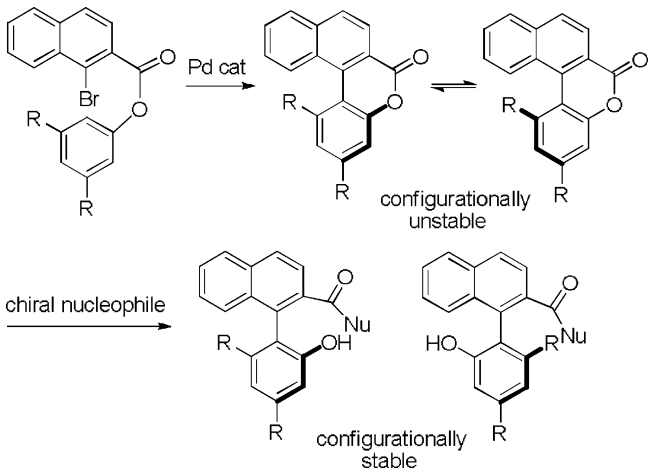
Scheme 5.

Intramolecular cyclization between two aryl units was first reported in 1982 when 3-bromo-4-phenylaminocinnoline was converted to indolo[3,2-c]cinnoline in 55% yield by heating in MeCN with triethylamine and ethyl acrylate at 150 °C under the catalytic action of $Pd(OAc)_2$ (Scheme 4) [23]. The reaction takes place only in the presence of an olefin such as ethyl acrylate probably because coordination of the latter facilitates reductive elimination from the metal [24].

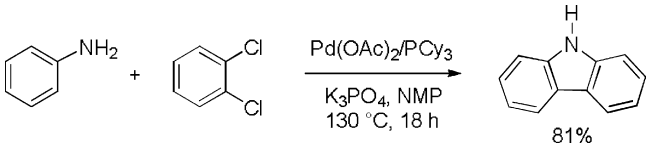
This type of cyclization was applied to several aryl halides *ortho*-bonded to an aryl group not only through an NH bridge but also through other bridges containing one or two heteroatoms [25]. Ames reported the Pd-catalyzed synthesis of dibenzofuran from *o*-bromophenyl phenyl ether in 74% yield by heating at 170 °C in DMA (*N*,*N*-dimethylacetamide) in the presence of Na_2CO_3 as a base (Scheme 5). The reaction is likely to proceed through an η^2- or η^1-arene coordinated species favoring C–H activation [26,27].

The procedure has been utilized for the synthesis of several natural products containing the biphenyl unit [28–34].

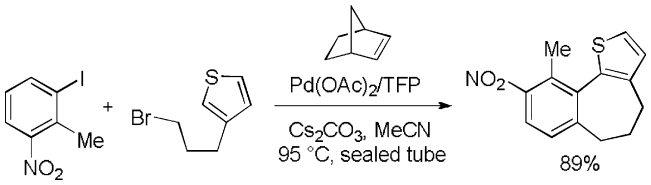
The direct Pd-catalyzed arylation is quite useful for the synthesis of configurationally unstable lactones (Scheme 6) which allow the atroposelective construction of axially chiral biaryl systems through nucleophilic attack on the lactone. The appropriate choice of the Pd catalyst precursor and the ligand depends on the steric hindrance of the substituents present in the aromatic rings [35].



Scheme 6.



Scheme 7.



Scheme 8.

Analogous intramolecular coupling reactions led to condensed dihydroazaphenanthrenes [36], naphthobenzazepines [37] pyrrolophenanthridine (alkaloids precursors) [38], and a porphyrin, containing a five-membered condensed ring, from bromotetraphenyl porphyrin [39].

Sequential Pd/P*t*-Bu_3 catalyzed amination of *o*-chloroanilines with bromoarenes and intramolecular coupling on the *ortho* C–H of the bromoderivative led to carbazoles. The natural alkaloid Clausine P (1,7-dimethoxy-6-methyl-9*H*-carbazole) was obtained in a one-pot reaction in 80% yield from 2-chloro-5-methoxy-4-methylaniline and 2-bromoanisole under microwave irradiation at 160 °C in toluene using $Pd(OAc)_2$, P*t*-Bu_3 and *t*-BuONa [40].

Recently another Pd-catalyzed domino reaction involving amination and direct C–H bond arylation to generate carbazoles from anilines and 1,2-dihaloarenes has been reported (Scheme 7) [41].

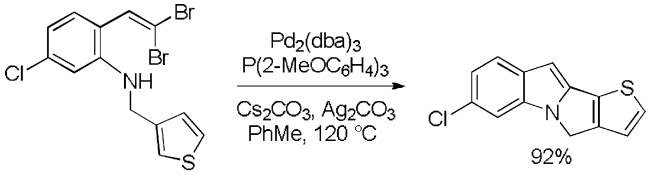
Pd-catalyzed domino reactions involving *ortho* alkylation of aryl iodides and direct arylation of indoles [42], pyrroles [43], thiophenes and furans [44] to produce polycyclic heterocycles have been described by Lautens' group. For example the seven-membered annulated ring product of Scheme 8 was obtained in 89% yield. The intramolecular heteroarylation is the last step of a sequence involving alkylation of palladacycles. Arylation via metallacycles is dealt with in Section 4.3.

An analogous strategy led to annulated 2*H*-indazoles and 1,2,3 or 1,2,4-triazoles [45a] and to many other condensed heterocycles [45b].

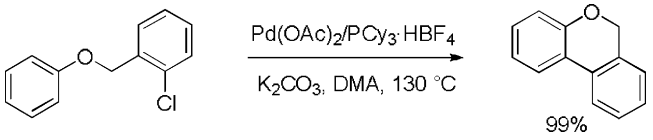
A variety of polycyclic thiophenes and benzothiophenes have been made accessible [45c].

According to a domino Pd-catalyzed amination/direct arylation strategy *o*-*gem*-dibromovinylaniline gives rise to an indolylpalladium species which reacts with heteroaromatic groups such as the thienyl one, linked to the indole nitrogen through alkyl groups, to form a new condensed ring. Tris(2-methoxyphenyl)phosphine in toluene with cesium carbonate as a base and silver carbonate as halide scavenger were required to obtain an optimal process (yields up to 92%) (Scheme 9) [45d].

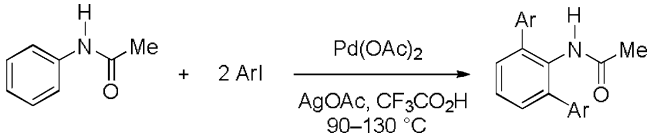
Another auto-tandem catalysis reaction leading to indoloquinolines and involving intermolecular Pd-catalyzed C–N and intramolecular arylation is due to Maes' group [45e].



Scheme 9.



Scheme 10.



Scheme 11.

Recently the direct intramolecular C–H arylation of arenes to generate a variety of five- and six-membered carbo- or heterocyclic biaryl compounds has been extensively studied. The ligand 2-(diphenylphosphino)-2′-(*N*,*N*-dimethylamino)biphenyl gave with Pd an efficient catalyst for intramolecular ring closure of aryl bromides *o*-linked to an arene through an ether or an amide group [46]. Using $Pd(OAc)_2/PCy_3{\cdot}HBF_4$ direct arylation of aromatic C–H bonds with chlorides, bromides and iodides was achieved (Scheme 10). Iodides were less reactive because of catalyst poisoning due to the accumulation of the iodide salts formed. This could be prevented by the addition of silver additives [47]. Aryl chlorides could be cyclized in high yields using electron-rich *N*-heterocyclic carbene ligands [48,49].

According to Fagnou's group $Pd(OH)_2/C$ (Pearlman's catalyst) is an excellent catalyst for arene direct intramolecular arylation reactions of aryl iodides and bromides. Moreover evidence was provided indicating that an active homogeneous Pd species is formed under the reaction conditions [50]. The significant kinetic isotope effect observed in many direct arylations points to the involvement of processes in which proton abstraction by a base (S_E3 process) or σ-bond metathesis are at work [46,47]. Progress in Pd-catalyzed direct C–H intramolecular activation in synthesis of biaryl derivatives has been reviewed [10].

As mentioned before these intramolecular cyclizations are likely to imply pre-coordination of the arene to be arylated to Pd through an η^2- or η^1-bond [26,27]. From this standpoint intramolecular reactions may be regarded as chelation assisted.

Intramolecular arylation of phenols to benzochromenes can also be achieved in dioxane at 140 °C in the presence of 2.5 equiv. of *t*-BuOH and without transition metals. Starting from a derivative of the substrate shown in Scheme 10, containing a hydroxyl group *meta* to the aryl C–O bond, the 1-hydroxy derivative of 6*H*-benzo[*c*]chromene was obtained (73% yield) along with its 3-hydroxy isomer. A benzyne intermediate appears to be involved [51].

4. Assisted intermolecular arene C–H arylation

This leads us to selective attacks on arene C–H bonds through intermolecular reactions. The need for the assistance of a chelating group [52], a heteroatom [53] or a metallacycle [54] has been recognized as far back as the eighties.

4.1. Arene C–H arylation assisted by chelation

The original work by Tremont, who reported the alkylation with alkyl iodide at the *ortho* position of acetanilide [55], has been extended to arylation [56]. A number of anilides as pivaloyl or acetyl derivatives have been arylated with aryl iodides to the corresponding 2,6-diarylanilides using palladium acetate as catalyst and stoichiometric silver acetate in trifluoroacetic acid at 90–130 °C (Scheme 11). High yields and turnovers up to 1000 have been attained. Benzamides [57] and benzylamines [58] have also been arylated analogously.

In the same category of reactions can be placed the arylation of benzodioxoles, which were treated directly using aryl bromides with $Pd(OAc)_2/Pt\text{-}Bu_2Me{\cdot}HBF_4$ in the presence of K_2CO_3 and Ag trifluoroacetate at 150 °C in DMA [10,47].

2-Arylpyridines [59], benzaldimines and aryloxazolines were readily arylated with good to excellent yields by both electron-rich and electron-poor aryl chlorides in NMP in the presence of $RuCl_3(H_2O)_n$ as catalyst. The double arylation of arylpyridine derivatives observed with aryl chlorides was prevented by using the less reactive aryl tosylates [10]. Aryl tosylates [60] have also been used [59,61] in Ru-catalyzed coupling assisted by an oxazoline group, phosphine oxides being the ligand of choice (Scheme 12). Phenols have been used directly adding a stoichiometric amount of *p*-tosyl chloride to effect tosylation [62].

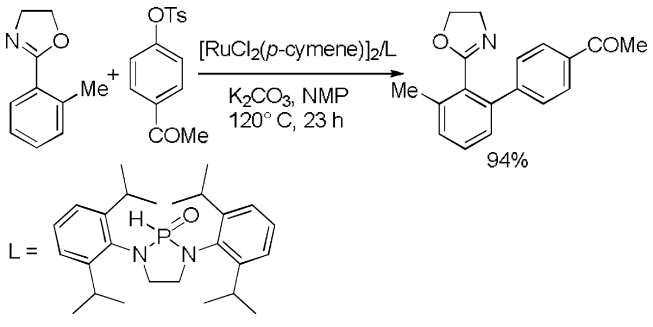
Previous work by Oi and Inoue described the ability of oxazolinyl or imidazolinyl substituents in the aromatic ring to direct Ru-catalyzed arylation towards the *ortho* position of the arene [63a]. According to Dixneuf and coworkers proton abstraction by carbonate is at work in the diarylation of 2-pyridylbenzene with aryl bromides using NHC-carbene/$RuCl_2$ as catalyst [63b]. Mesitylcarboxylic acid was shown to act as co-catalyst in assisted Ru-catalyzed arene arylations in apolar solvents. A deprotonation mechanism [64] analogous to the one mentioned above [18,19] appears to be operative.

Aryloxazolynyl ligands have been used to direct *o*-arylation in stoichiometric Grignard reactions with arylmagnesium halides [65]. The oxazolinyl group can be easily converted into a carboxylic function.

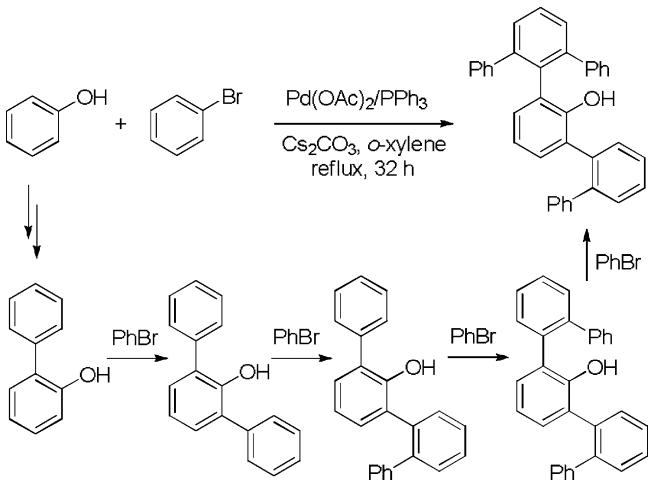
Miura's group [9,52] used phenols to direct Pd-catalyzed arylation at the *ortho* position. For example the reaction of phenol with bromobenzene in the presence of $Pd(OAc)_2/PPh_3$ as catalyst with Cs_2CO_3 as a base in refluxing *o*-xylene for 32 h gave 2-biphenyl-6-terphenylphenol in 58% yield. One of the possible pathways is shown below in Scheme 13. Benzyl alcohols, acetophenones, benzyl phenyl ketones, anilides [9] and benzaldehydes [66] were arylated analogously in *ortho* positions. Aliphatic carbons of acetophenones and benzyl phenyl ketones were also arylated [9].

The mechanism seems to correspond to an electrophilic substitution assisted by chelation (Scheme 14). This is in accord with the transition state proposed for electrophilic attack on phenols [67].

Two methods for direct *o*-arylation of benzoic acids with aryl iodides or bromides have been proposed by Daugulis: the first employs stoichiometric amounts of silver acetate for iodide removal from aryl iodide in acetic acid at 130 °C; the second, suitable for aryl chlorides, uses *n*-butyl-di-1-adamantylphosphine ligand in DMF at 145 °C [68a]. Here the carboxylic group plays the role of assisting arylation [68b].



Scheme 12.



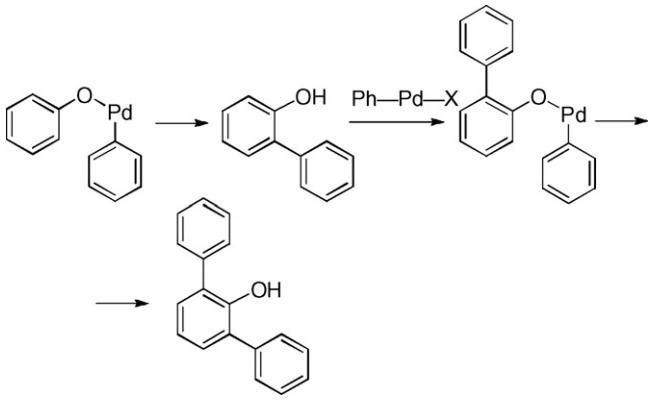
Scheme 13.

4.2. Arene C–H arylation directed by heteroatoms

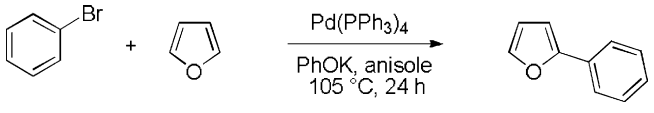
The attack of bromobenzene on the 2-position of furan has been recognized since 1985 [53] (Scheme 15) but only more recently a methodology of broader scope has been worked out.

A number of heterocycles can now be arylated, in general through electrophilic mechanisms, selectively at the heteroatom activated C–H bond, using Pd and Rh catalysts. Beside furans [69], several types of heterocycles such as pyrroles [70], indoles [70,71], thiophenes [9], oxazoles [72], thiazoles [50], imidazoles [73], indolizines [74] undergo selective arylation [9]. Scheme 16 shows some examples using different heterocyclic substrates, aryl halides (iodides, bromides, chlorides), catalysts, bases and additives.

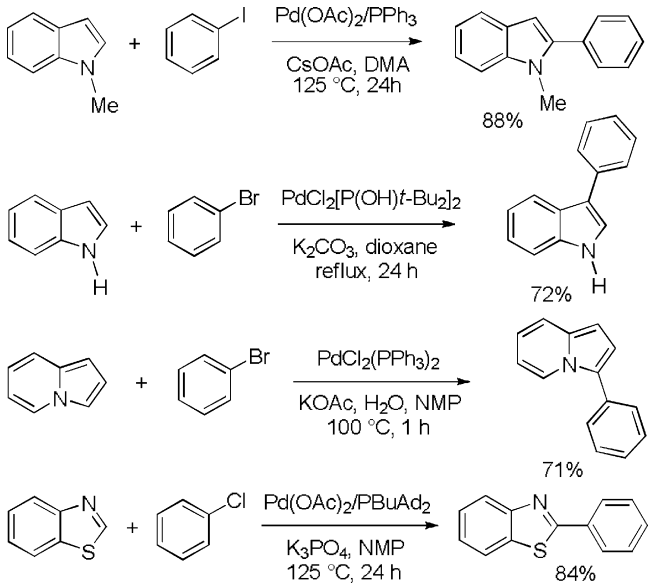
Indoles offer an interesting example of reactivity at two positions (C-2 and C-3). See for examples the first and second equation of Scheme 16. Reactivity at C-3 was obtained in the presence of phosphinous acids as ligands for Pd [71] while phenylation at the C-2 position occurred in the presence of $Pd(OAc)_2/PPh_3$ [75]. Sames et al. rationalized this behavior in the framework of the electrophilic substitution mechanism. Position C-3 is the preferred one, but if proton removal from the initial Pd complex is slow, there is time



Scheme 14.



Scheme 15.



Scheme 16.

for a metal migration from C-3 to C-2 and arylation of the latter may occur exclusively [75]. In the absence of added ligand and in the presence of silver carboxylates, generated from Ag_2O, indoles are selectively arylated at the 2-position [76a]. Indole research has been reviewed [76b]. In the presence of $PdCl_2(PPh_3)_2$ and under the conditions reported in the third equation indolizine readily reacts with bromobenzene to afford the C-3 phenylated derivative in 71% yield. The reaction is compatible with a variety of substituents both on the indolizine and aryl halide [74]. The use of $AgNO_3$/KF at 150 °C allowed Pd-catalyzed arylation of 2-bromothiophenes with aryl iodides without affecting the Br–C bond [74c].

Pearlman's catalyst is also active in selective intermolecular arylations at C-5 of thiazoles [50].

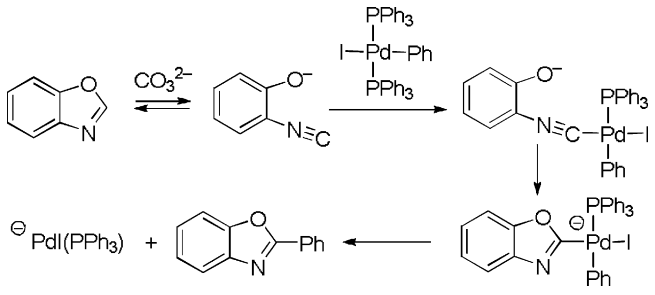
Aryl chlorides arylate benzothiazole (fourth equation of Scheme 16) under the catalytic action of Pd in the presence of bulky, electron-rich phosphine ligands such as *n*-$BuAd_2P$ (Ad = adamantyl), which gives the best results. The methodology is applicable to a variety of electron-rich heterocycles and aryl chlorides [72b]. Arylation of 2-arylthiazoles occurs at the 5-position using water as the reaction medium, with Pd/phosphine catalysts in the presence of silver carbonate [72c].

Selectivity in cross-coupling of azoles with two or more heteroatoms is discussed in a review [77]. Direct arylation of heteroarenes such as benzoxazoles was effected with tosylates in the presence of a dialkylbiarylphosphine (Buchwald's ligand [78b]) [78a]. Arylation of 1,2,3-triazole with aryl halides was performed under Pd [78c,79] and Cu [80] catalysis. Selective arylations at the 2- and 5-positions of azoles were achieved by varying the Pd-based catalytic system. For example CuI addition directed arylation towards position 2 of both *N*-methylimidazole and thiazole, while in the absence of CuI the 5-position was preferred [81].

Some SEM-protected pyrazoles (SEM = 2-(trimethylsilyl) ethoxymethyl) were arylated selectively at the 5-position and sequentially in the 3-position after SEM shift to the other nitrogen in the presence of palladium acetate, P(*n*-Bu)Ad_2 and potassium pivalate at 140 °C in DMA. The deprotonation mechanism [18,19,82] may be here at work to explain the preferential reactivity of the more acidic 5-position [83].

In some cases it has been shown that deprotonation with ring opening is involved.

Benzoxazoles open up the oxazole ring forming a palladium-coordinated isocyanophenolate [84]. The reaction occurs at 120 °C



Scheme 17.

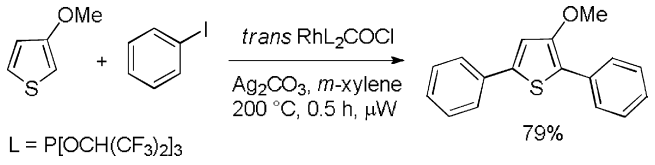
using $Pd(OAc)_2/PPh_3$, Cs_2CO_3 in DMF for 1 h. A proton abstraction mechanism has been suggested to be at work as shown in Scheme 17. A similar mechanism has been shown to be operative for 2-metalated thiazoles and imidazoles [85].

Thiophenes, furans, pyrroles and indoles were arylated with a Rh catalyst containing $P[OCH(CF_3)_2]_3$ as ligand. 3-Methoxythiophene was diarylated by iodobenzene selectively at carbons adjacent to sulfur to afford 2,5-diphenyl-3-methoxythiophene in 79% yield (Scheme 18). The reaction was over in 30 min when carried out in *m*-xylene at 200 °C under microwave irradiation [86]. The reaction was also extended to arene derivatives. Experimental data are consistent with an electrophilic mechanism [87].

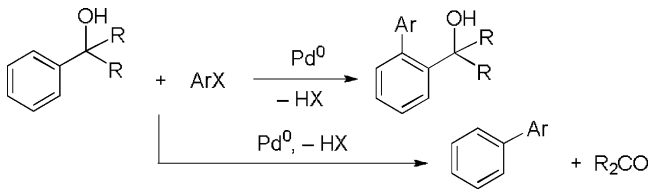
Rh-catalyzed arylation of benzimidazole in the presence of 9-cyclohexylbicyclo[4.2.1]-9-phosphanonane (cyclohexylphobane) was achieved by direct coupling of benzimidazole with aryl iodides and bromides bearing a wide variety of functional groups in good yields under microwave conditions (250 °C) [88].

Miura described several procedures in which arene and heteroarene C–H [6] and C–C [9] activation are intertwined. We deal first with the general process of arene arylation depicted in Scheme 19 for α,α-disubstituted arylmethanols, which can be traced to both type of activation, the former product coming from OH assisted C–H arylation and the latter from C–C bond cleavage with concomitant ketone formation (involving hydroxy palladation) [89].

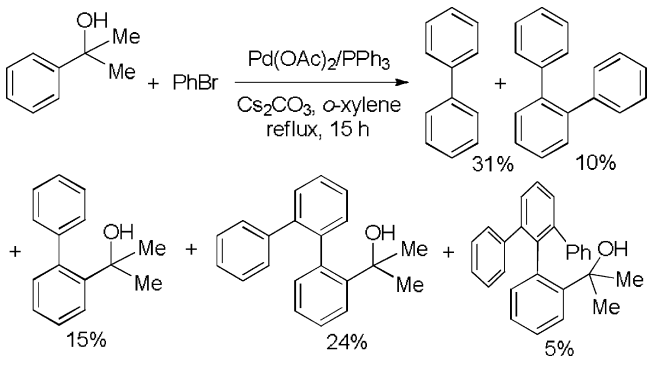
The reaction of 2-phenyl-2-propanol with bromobenzene gave rise to mono-, di- and tri-phenylated products as shown in Scheme 20. The first two products result from arylation via C–C bond cleavage, while the others from OH assisted C–H arylation. Selectivation towards the former products (essentially the monoarylated one) can be achieved using triphenylmethanol in place of 2-phenylpropanol and a bulky phosphine such as PCy_3. This also enables aryl chlorides to react efficiently [89].



Scheme 18.



Scheme 19.



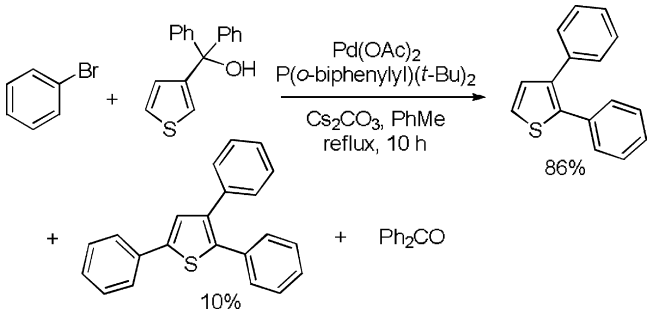
Scheme 20.

Passing to a heterocyclic substrate such as thiophene, the CR_2OH group was readily removed from the 3-position and replaced by a phenyl group after aryl attack on position 2. A third phenyl group attacked position 5 more slowly. Thus, as shown in Scheme 21, α,α-diphenyl-3-thiophenemethanol and bromobenzene were converted into 2,3-diphenylthiophene in 86% yield. Only a minor amount (10%) of 2,3,5-triphenylthiophene was formed [90].

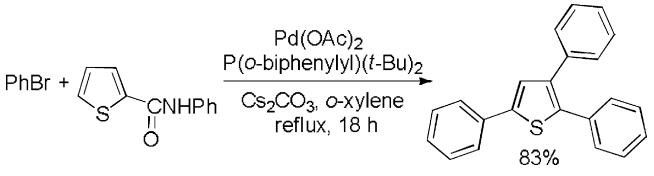
The first initial attack on the 2-position has been attributed to the assistance of the 3-methanol group while the second attack, replacing the methanol group itself, has been proposed to imply the formation of an –O–Pd–Ar group on the methanol substituent which assisted the electrophilic arene C–H activation. Another electrophilic attack involved position 5.

When a CONHR substituent was present in position 2 of thiophene position 3 was first phenylated likely through the assistance of the amide group. The resulting compound was either phenylated at position 5 or decarbamoylated. Decarbamoylation also occurred in the 3,5-diphenylated compound. Both products were further phenylated or diphenylated to give 2,3,5-triphenylthiophene in good yield (Scheme 22) [91].

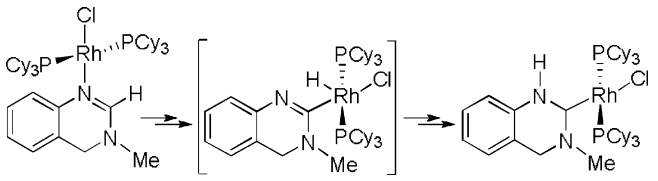
If an appropriate substituent such as CN was present at thiophene C-3 even the 4-position could be phenylated through C–H activation. Thus the reaction of 3-cyanothiophene, carried out under the conditions of Scheme 22 for a period of 70 h, gave 3-cyano-2,4,5-triphenylthiophene in 65% yield. The presence of substituents in the bromobenzene significantly affected the



Scheme 21.



Scheme 22.



Scheme 23.

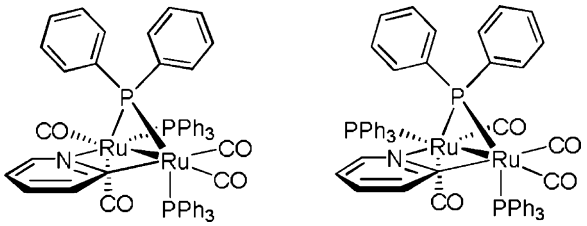


Fig. 1. Pyridine C–H activation by coordination to a binuclear complex.

amount of product formed (78% yield with 3-$CF_3C_6H_4Br$; 48% with 4-$MeOC_6H_4Br$) [91].

The selectivity problem was addressed by Steglich and coworkers [92] and by Forgione et al. [69]. According to the latter authors 2-heteroarylcarboxylic acids direct arylation towards replacement of the COOH group [68b]. This process occurred selectively in the presence of an R substituent in 3 position. If 3 was not substituted arylation in 3 occurred in part by assistance of the COOH group and the resulting 3-aryl-2-carboxylic derivative underwent a new arylation with replacement of the carboxylic group [69a]. Perarylation of 3-thiophene and 3-furanecarboxylic acids has been reported [93a]. 2,5-Disubstituted furans undergo Pd-catalyzed arylation with aryl bromides at C-4 [93b].

Imidazo[1,5-*a*]pyrazines have been arylated at C-5 with palladium acetate in DMF at 120–130 °C, using cesium carbonate as a base and $(t\text{-Bu})_2PMe{\cdot}HBF_4$ as ligand. A Heck-type mechanism has been proposed [93c].

Aryl iodides selectively arylate purines at C-8 in the presence of Pd(0) as catalyst and more than the stoichiometric amount of CuI, with cesium carbonate as a base [93d].

A phosphine and Cu free Pd-catalyzed procedure using pivalic acid as additive has been recently reported to be valid for *N*-heterocycles [93e].

Arylation of electron-deficient aromatics of azine type appears more difficult. According to Bergman, Ellman and coworkers in the catalytic arylation of quinolines and pyridines [94a] and azoles [94b,c] *ortho* to nitrogen, rhodium(chloro)carbonyl dimer and a Rh tetrahydrophosphepine complex have been used as catalysts at 175–190 °C. Using 3-methyl-3,4-dihydroquinazoline as model they gathered evidence that Rh first coordinates to nitrogen before C–H activation leading to a carbene species (Scheme 23) [94d].

Carmona and coworkers [95] and Esteruelas et al. [96] have proposed analogous C–H activation mechanisms for Ir, Os and Ru complexes. Rh(I) also catalyzes arylation via decarbonylation of benzoic anhydride [97].

A Cu(I)-catalyzed procedure which is valid both for electron-poor and electron-rich heterocycles has been developed [98] using K_3PO_4 or lithium alkoxide as a base and DMF or DMF/xylenes as solvent [99]. 5-Aryl benzotriazepines have also been obtained by direct arylation [100]. Phenanthroline is the ligand of choice.

Coupling of heteroarenes and aryl halides or triflates to biaryls has been achieved with nickel acetate complexed with bipyridine or diphenylphosphinoferrocene [101]. Nickel also catalyzes arylation of azoles with aryl bromides [102].

As to arylation of azine-type heterocycles, $Ru_3(CO)_{12}$ in the presence of PPh_3 and Cs_2CO_3 catalyzes the arylation of pyridine with iodobenzene to give a mixture of 2-, 3-, and 4-phenylpyridines (7:2:1) in 62% yield working in pyridine as solvent. In the effort to identify the catalyst resting state a mixture of two dimers was discovered. As shown in Fig. 1 these species activate pyridine through bridging the two Ru atoms, but unfortunately are not active as catalysts [103].

A clever way to cause difficult to arylate heteroarenes to react with aryl bromides to form the 2-arylated products has been reported [104]. It consists of using *N*-oxides such as those of pyridine, pyrazine, pyridazine, pyrimidine and quinoxaline as substrates. The products can be deoxygenated to generate the arylated azines by Pd-catalyzed hydrogenolysis. Pyrimidine *N*-oxide exhibited an inhibiting action which could be overcome by adding stoichiometric amounts of CuCN or CuBr. Diazines reacted faster than pyridines. The reactivity of thiazoles and imidazoles is remarkably enhanced in the order C-2 > C-5 > C-4. A concerted palladation-deprotonation has been postulated for C–H activation [22c] in view of the sensitivity of the reaction to C–H acidity (Scheme 24). This mechanism has been shown by theoretical calculations to account also for reactions of electron-rich arenes [21a].

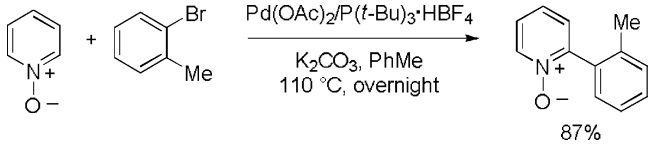
If an azole and an azine ring are fused as in 6- and 7-azaindoles the azine ring can be induced to react preferentially by previously forming its *N*-oxide [105].

A comprehensive outlook on the subject of *N*-oxide arylation has recently appeared [104b].

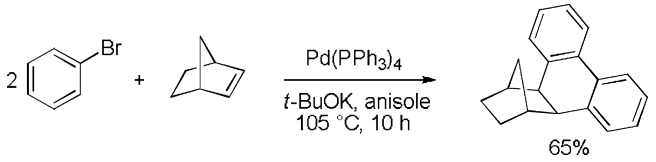
U(IV) and Th(IV) alkyl complexes are able to activate an *ortho* C–H bond in pyridine *N*-oxide by cyclometalation [106].

4.3. Metallacycle-assisted arene C–H arylation

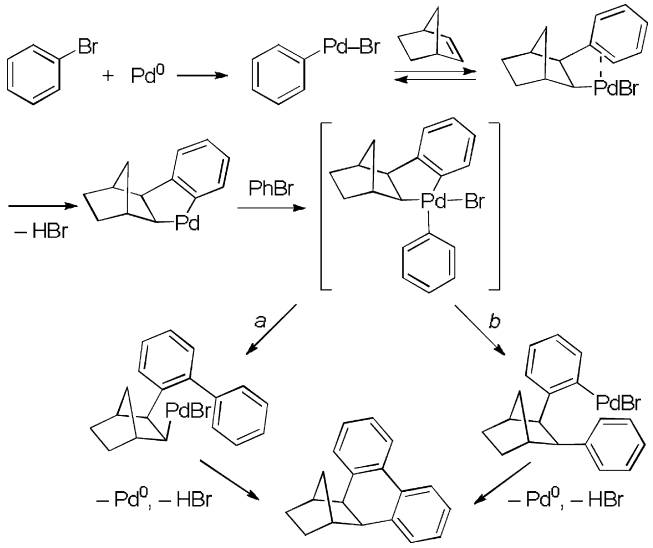
A complex reaction leading to a methanotriphenylene (Scheme 25) was described in 1985 [54]. Bromobenzene and norbornene reacted in anisole at 105 °C under the catalytic action of $Pd(PPh_3)_4$ and in the presence of *t*-BuOK giving a 65% yield of *cis*,*exo*-hexahydromethanotriphenylene. The reaction consists of a series of steps starting from the oxidative addition of bromobenzene to Pd(0) to form the phenylpalladium complex, which undergoes stereoselective norbornene insertion to *cis*,*exo*-phenylnorbornylpalladium bromide with the metal center weakly bound to the aromatic ring through an η^2 coordination as shown by X-ray analysis [26,27d]. This complex is rather stable towards β-H elimination due to the lack of β-hydrogen *syn* to Pd. This circumstance prevents the occurrence of a Heck-type reaction under the conditions used and favors an alternative pathway leading to arene C–H activation to afford the five-membered alkylaromatic palladacycle. The latter directs the attack of a molecule of bromobenzene either on the phenyl (way a) or the norbornyl moiety (way b) possibly through the intermediacy of a Pd(IV) species (isolated



Scheme 24.



Scheme 25.



Scheme 26.

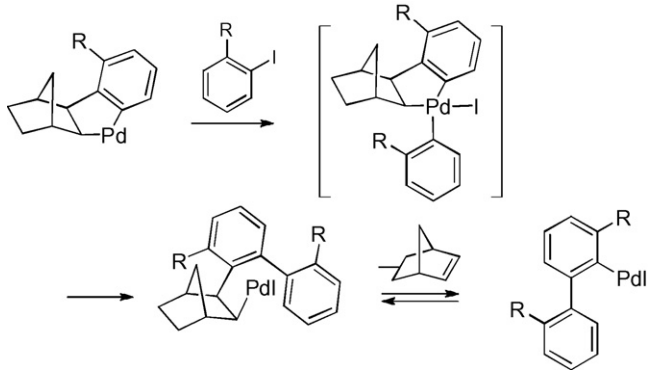
with benzyl bromide [107]) in place of bromobenzene. Final ring closure by C–C coupling then occurs both on the norbornyl and the aryl moiety (Scheme 26).

Way *a* leads to an electrophilic alkylation, while way *b* involves an arylation for which the previously mentioned proton abstraction mechanism [19,21a,22] may be invoked.

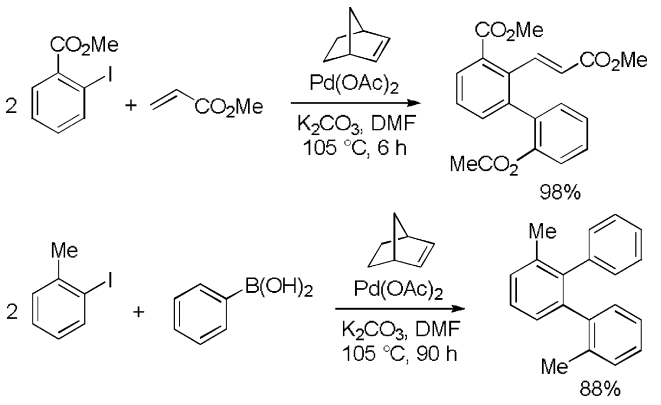
That two pathways (*a* and *b*) are at work was proved by introducing a *para* substituent in the starting bromobenzene, which gave two differently substituted methanotriphenylenes. Thus the aryl–aryl coupling was not selective.

Further study led to the discovery that in the presence of an *ortho* substituent in the aryl halide the reaction proceeds selectively according to path *a*, only the aryl–aryl bond and not the aryl–norbornyl bond being formed [108]. This is likely due to the steric effect exerted by the *ortho* substituent which favors the attack at the aryl site of the alkylaromatic palladacycle. Owing to the sterically hindered situation created by the two *ortho* substituents, the resulting complex readily deinserts norbornene, thus giving rise to a biphenylylpalladium complex which can be caused to react with different partner molecules according to the known reactivity of arylpalladium species. Norbornene expulsion implies a β-C–C bond cleavage, norbornene being not incorporated in the final product (Scheme 27).

Causing the biphenylylpalladium complex to undergo a reaction able to liberate the organic product and Pd(0) makes the process catalytic. Thus selectively substituted biphenyls have been synthesized by reaction with a hydrogen donor such as benzyl alcohol;



Scheme 27.



Scheme 28.

biphenyl derivatives containing a vinyl or an oxoalkyl chain by reaction with an acrylic ester or an allylic alcohol, respectively [109]; phenanthrenes by reaction with diarylalkynes [110] and terphenyls by reaction with arylboronic acids [111]. Scheme 28 reports two examples.

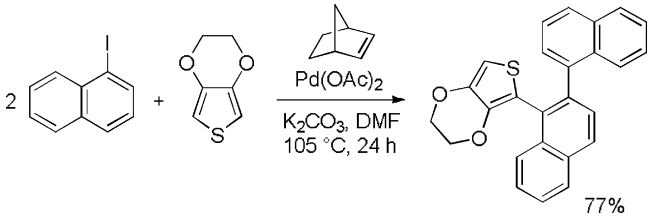
The problem of delaying the termination step until the end of the stoichiometric sequence to prevent competitive reactions in earlier steps is common to all these reactions but it is particularly critical for hydrogenolysis [109a].

More recently termination of the reaction sequence has been achieved by C–H arylation of a heteroarene (Scheme 29) [112].

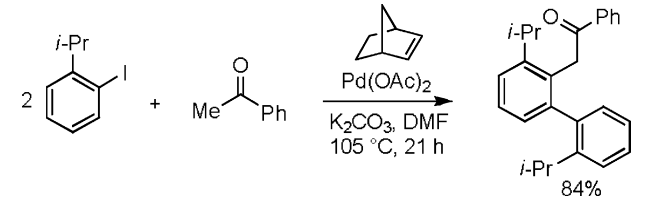
The presence of norbornene thus deviates the direct attack of the iodoarene on the C–H adjacent to the heteroatom shown in Scheme 16 towards the formation of the biphenyl unit before final C–H arylation.

C–H activation of aliphatic species such as ketones in the termination step has also been achieved (Scheme 30) [113].

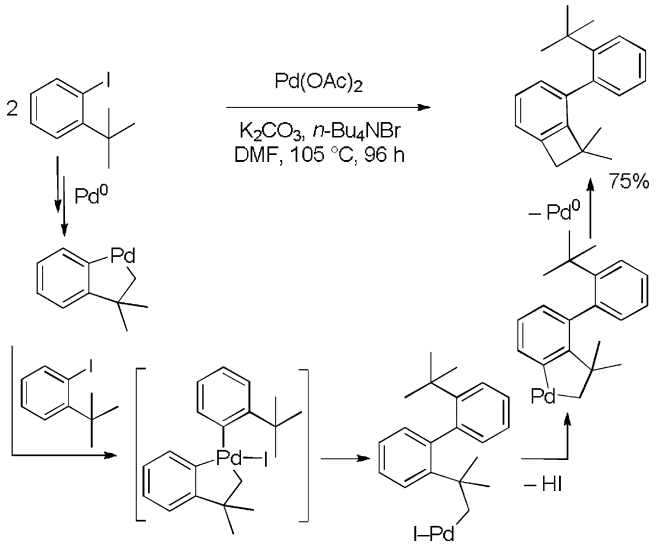
We can place in the general framework of metallacycle-assisted aryl coupling Dyker's findings that *o*-*t*-butyliodobenzene [114] and *o*-iodoanisole [115] undergo aryl coupling through palladacycle formation. As shown in Scheme 31 *o*-iodo-*t*-butylbenzene reacts with Pd to give an alkylaromatic palladacycle through initial oxidative addition followed by cyclometallation of an unactivated sp^3 carbon. A second molecule of *o*-iodo-*t*-butylbenzene reacts selectively with the metallacycle thus formed, possibly through the intermediacy of a Pd(IV) species, to afford a Pd complex containing a biaryl structure. The latter undergoes a second cyclometallation, followed, this time, by reductive elimination to the organic product.



Scheme 29.

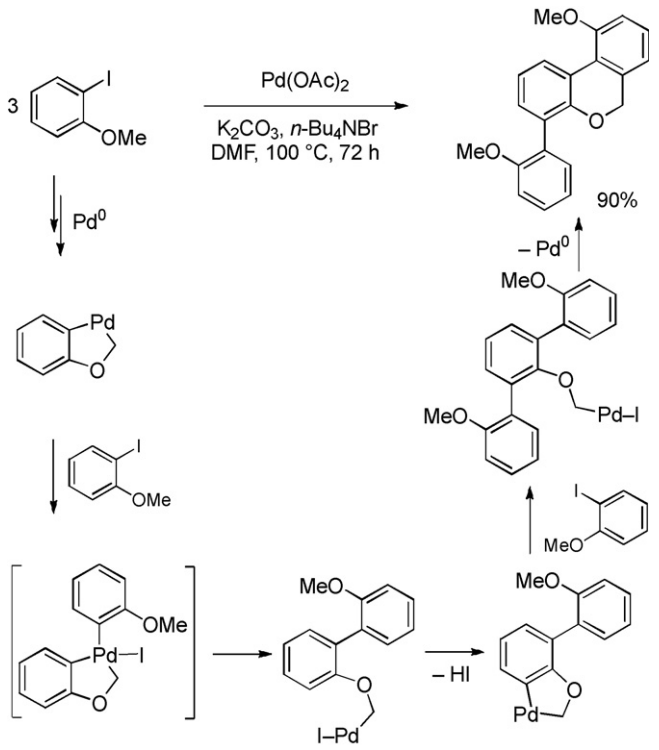


Scheme 30.

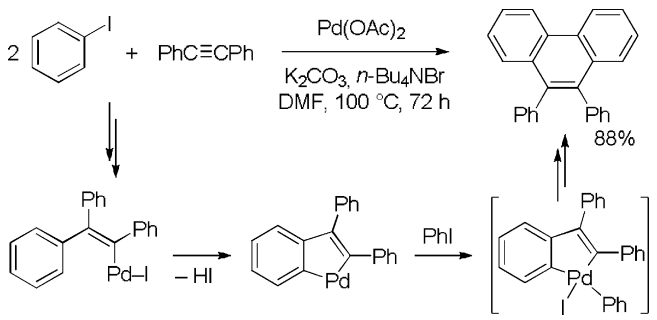


Scheme 31.

o-Iodoanisole behaves in a similar way combining three aromatic units to generate the selectively substituted dibenzopyran derivative reported in Scheme 32 in 90% yield. The described reaction pathway is similar to the previous one up to the formation of the second metallacycle which, in place of undergoing reductive elimination to a four-membered-ring, repeats the reaction with a new molecule of *o*-iodoanisole to give a new metallacycle, which finally reductively eliminates the dibenzopyran derivative. Interestingly, the palladacycles initially involved in these reactions have been isolated with stabilizing ligands [27a,116]. That the main product results from the reaction of three molecules of iodoanisole instead of the two involved in the case of *o*-iodo-*t*-butylbenzene can be attributed to the different tendency to close a 4-membered ring in the two cases. In fact the geminal substituent effect favors



Scheme 32.



Scheme 33.

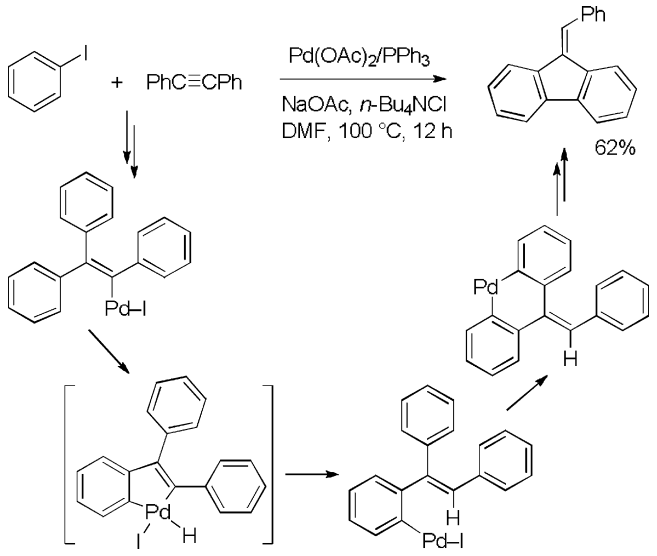
competitive ring closure in the former, thus interrupting the sequence.

The palladacycles involved in Dyker's reactions behave similarly to the ones containing the norbornyl unit, readily reacting with aryl halides at the aromatic carbon–palladium bond. However in contrast with norbornene the isobutene or the formaldehyde molecules are not expelled in the presence of two *ortho* substituents. Isobutene could be removed in a stoichiometric reaction [27b].

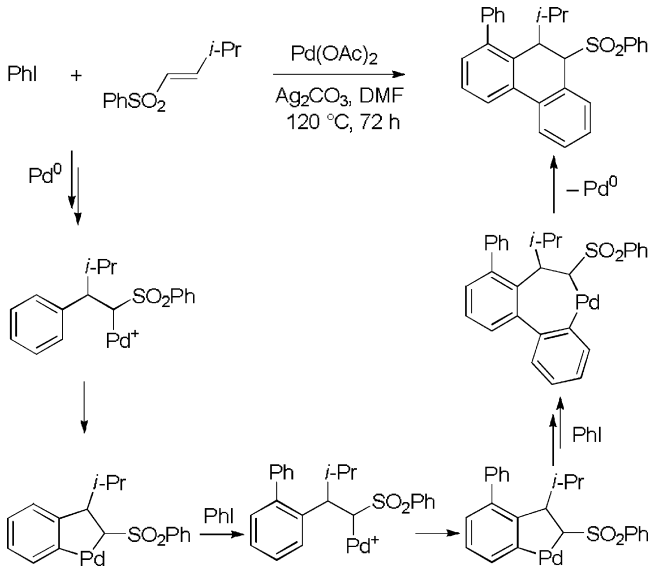
An intermediate palladacycle formation could also be obtained using iodobenzene with diphenylacetylene. It has been shown that the outcome of the reaction is strongly dependent on the base used. Dyker obtained 9,10-diphenylphenanthrenes using K_2CO_3 as a base in a 2:1 annulation reaction (Scheme 33) [117] while Larock synthesized 9-benzylidenefluorenes by performing a 1:1 reaction in the presence NaOAc (Scheme 34) [118].

In Larock's synthesis: the cyclopalladated precursor of benzylidenefluorene originates from the Pd migration from one site to another (Scheme 34). This aspect will be considered later in the context of Pd migrations.

Other unsaturated substrates undergo similar Pd-catalyzed arylation reactions. α,β-Unsaturated phenylsulfones react with aryl iodides in the presence of $Pd(OAc)_2$ as catalyst and Ag_2CO_3 as a base to give 9-phenylsulfonyl-9,10-dihydrophenanthrenes. The proposed reaction pathway implies double bond arylation, palladacycle formation, double phenylation with iodobenzene and final ring closure to give the observed dihydrophenanthrene derivative. The presence of the sulfone group in the σ-alkylpalladium intermediates is likely to disfavor β-H elimination, thus making possible the



Scheme 34.

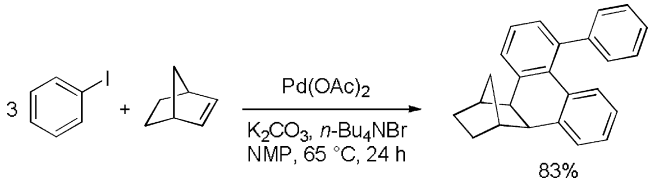


Scheme 35.

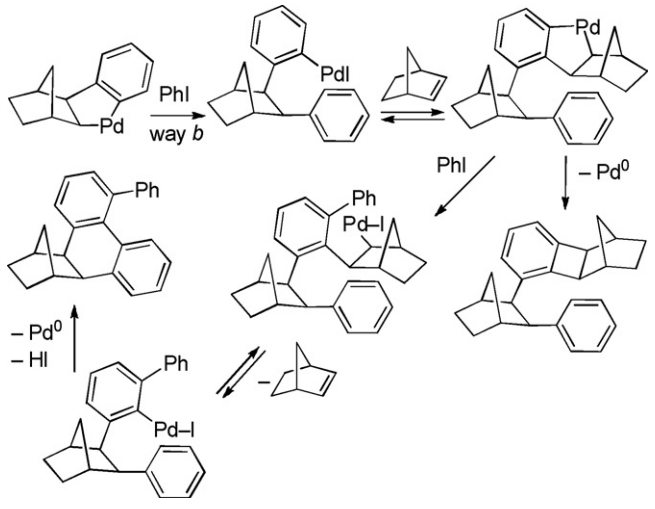
intramolecular aromatic C–H activation process with formation of the five-membered palladacycle (Scheme 35) [119].

De Meijere [120] has further reported that the reaction of iodobenzene and norbornene of the type shown in Schemes 25–26 takes a different course leading to the formation of a 3:1 coupling product (Scheme 36).

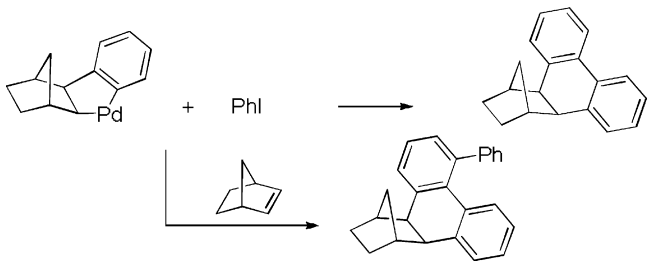
This helps to throw light on palladacycle behavior. According to way *b* of Scheme 26 the initial palladacycle gives rise to a species which is not particularly prone to cyclization in the presence of norbornene and prefer to undergo another norbornene insertion. This has been proved [109a] by the isolation of the corresponding benzocyclobutene product (Scheme 37).



Scheme 36.



Scheme 37.



Scheme 38.

If now the first and the second palladacycle of Scheme 37 are compared the situation turns out to be quite similar with the only difference that an alkyl (2-phenylnorbornyl) group in *ortho* to the aromatic to aliphatic C–C bond of the palladacycle is present in the latter.

In the presence of iodobenzene the palladacycle does not give rise to reductive elimination to a benzocyclobutene [109a] but undergoes functionalisation at the aryl site, the *ortho* substituent clearly causing preferential palladacycle opening according to Scheme 37.

Further evidence was gained by comparing conditions for the formation of hexahydromethanotriphenylene and phenylhexahydromethanotriphenylene. The former was obtained selectively by causing the initial palladacycle to react with iodobenzenze in the absence of norbornene while the latter was obtained only in the presence of norbornene, in agreement with the proposed mechanism (Scheme 38) [108].

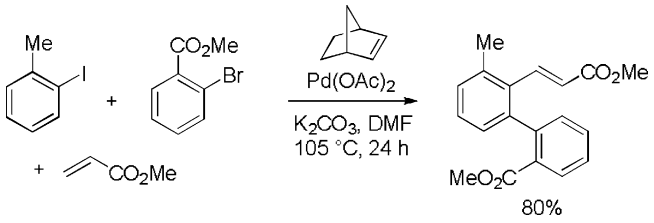
The Pd intermediate formed by norbornene expulsion in a catalytic reaction involving iodobenzene and norbornene (KOAc as a base in DMF at 105 °C) has been trapped by adding olefins such as methyl acrylate or styrene [109a]. This is another instance of the extremely versatile behavior of the reactions via metallacycles with more than two components.

The reaction of Scheme 25 was extended by de Meijere to other norbornene-type strained olefins such as deltacyclene, norbornenol, norbornenone and dicyclopentadiene [120b]: also indene gave 1:3 coupling products analogous to the ones from norbornene but with different regiochemistry [121]. The use of heterocyclic aryl iodides such as iodothiophenes and iodopyridines led to interesting products although in moderate yields. The reaction of norbornene and *m*-iodopyridine gave the corresponding bipyridine derivative. The reaction required higher temperature and the addition of triphenylphosphine [120b].

In many of the reactions shown so far the unsaturated compound needed for metallacycle formation is retained in the final product whereas with norbornene, norbornadiene and similar rigid olefins it is possible to find conditions to liberate it again concomitantly to aryl to aryl coupling. Even if usually present in substantial concentration to favor their insertion, these olefins act catalytically jointly with Pd catalyst. This is a remarkable feature in catalysis in that an organic and an inorganic catalyst work in cooperation.

All these reactions involve C–C coupling to biaryls starting from the same aryl halide. Different aryl halides couple selectively provided that *o*-alkyl-substituted aryl iodides are reacted with aryl bromides and in certain cases also chlorides, containing electron-withdrawing substituents. The syntheses are carried out in one-pot under mild conditions starting from easily available reagents (Scheme 39) [122].

The reaction pathway is analogous to the one shown in Scheme 26, way a, but it implies the selective formation of the initial palladacycle at the expenses of the more reactive aryl iodide. At this point further attack on the palladacycle only occurs by the bromide. The highly preferred reaction of this compound is not easy



Scheme 39.

to explain but it is likely to be due to steric effects. Further study is required to clarify this point, which is also associated with the possible formation of a Pd(IV) complex. Reductive elimination from the latter followed by norbornene deinsertion, gives a biphenylylpalladium complex from which a Heck-type reaction liberates the Pd(0) catalyst and the organic product shown in Scheme 39.

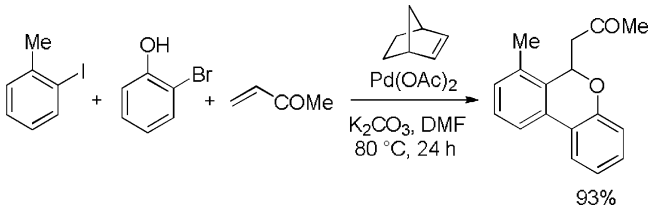
The reaction is tolerant of several functional groups which can be further exploited for ring formation. As shown in Scheme 40 the reaction of *o*-bromophenol with *o*-iodotoluene and methyl vinyl ketone led to the formation of the corresponding dibenzopyran derivative in high yield (93%). The cyclization step is triggered by the *o*-hydroxyl group appropriately positioned for an easy attack on the activated double bond through Michael reaction. In spite of the fact that the most effective substituents on the aryl bromide are the electron-withdrawing ones *o*-bromophenols react satisfactorily, likely because of the positive chelating effect of the *o*-hydroxyl group [123].

N-Sulfonylated 5,6-dihydrophenanthridines have been prepared analogously but under different conditions also involving the use of sulfonamides [124].

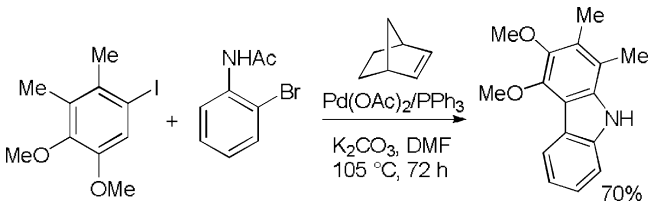
Working in the absence of Michael acceptors carbazoles have been obtained, for example 2-ethylcarbazole in a 98% yield. The antibiotic carbazomycin A has been synthesized from the pertinent iodide and *N*-acetylated *o*-bromoaniline (Scheme 41) in a 70% yield [125].

6-Phenanthridinones and their heterocyclic analogues were synthesized through sequential aryl–aryl and *N*-aryl coupling. Using 3-bromothiophene-2-carboxylic acid methylamide in the reaction with *o*-iodotoluene in the presence of $Pd(OAc)_2$/TFP, and norbornene as catalyst, K_2CO_3 as a base in MeCN at 85 °C, the corresponding quinolinone derivative was isolated in 80% yield (Scheme 42) [126].

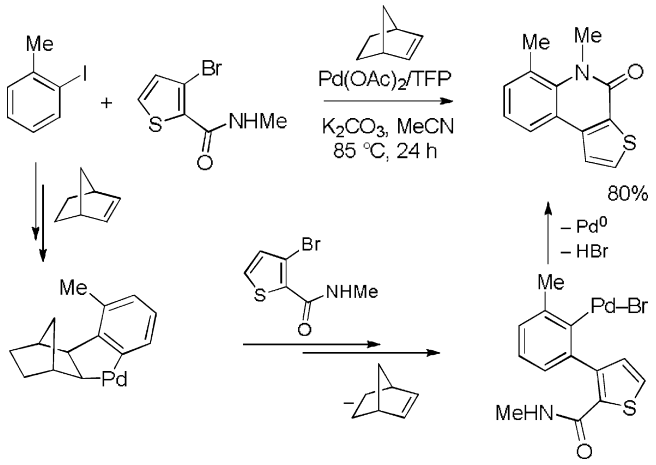
A report on reactions involving the Pd/norbornene dual catalysts has recently appeared [109b].



Scheme 40.



Scheme 41.



Scheme 42.

Under similar conditions in the absence of norbornene *o*-bromoaromatic carboxamides undergo homocoupling reaction with concomitant decarbamoylation to afford condensed pyridones. 3-Bromo-1-metil-1H-indole-2-carboxylic acid methylamide reacted in the presence of $Pd(OAc)_2$/TFP as catalyst, K_2CO_3 as a base in DMF at 105 °C to give the corresponding pyridine in 71% yield [127]. The reaction has been proposed to proceed through palladacycle-catalyzed homocoupling of the bromoamide followed by splitting of the aminocarbonyl group by intramolecular *ipso* aromatic substitution.

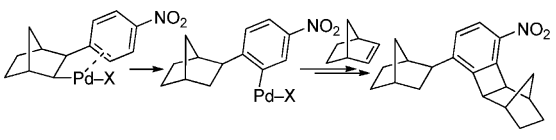
The Pd-catalyzed reaction of *o*-bromobenzamides to phenanthridinones with concomitant decarbamoylation was first reported by Caddick and Kofie [128]. A similar reaction using a catalytic system based on $Pd(OAc)_2$/2-(8-methoxy-1-naphthyl)phenyldiphenylphosphine and Cs_2CO_3 as a base has been recently shown to give the same products with expulsion of isocyanate derivatives [129].

5. Palladium migration in arenes

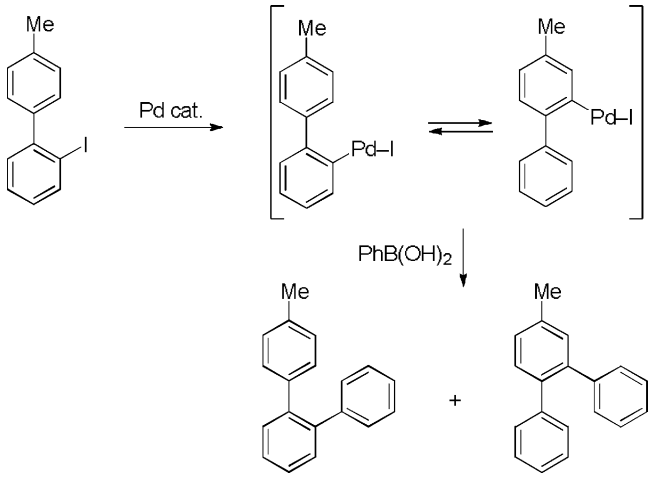
An interesting aspect of the chemistry of aryl coupling is that the aryl coupling can take place at an arene position different from that of the original C–Pd bond. That Pd could move from one side to the other of a palladacycle (from sp^3 to sp^2) had been previously shown in the case of norbornene [130]. The methanobiphenylene derivative reported in Scheme 43 was obtained by reaction of 4-nitrobromobenzene with norbornene in anisole at 105 °C under the catalytic action of $Pd(PPh_3)_4$ and in the presence of KOAc. Other examples of sp^3–sp^2 migrations have been recently reviewed [131].

According to Gallagher [132] and Larock [133] Pd migrates along arene or heteroarene nuclei and the corresponding complexes react with ethyl acrylate to give the respective isomers. Recently the isomeric Pd intermediates have been trapped by Suzuki cross-coupling using arylboronic acids (Scheme 44) [134].

This possibly involves an intermediate palladacycle and is relevant to the aryl coupling process. Pd migration can be made selective using aromatic C–H bonds of sufficiently different acidity in the two rings. Migration occurs towards the more acidic



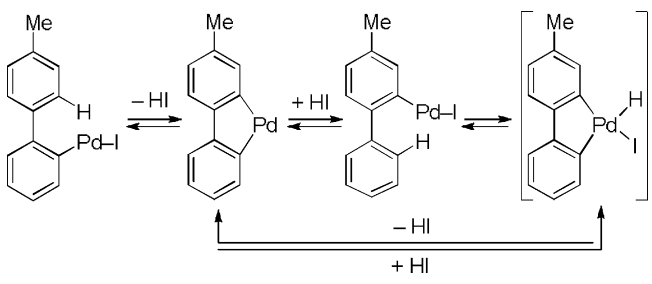
Scheme 43.



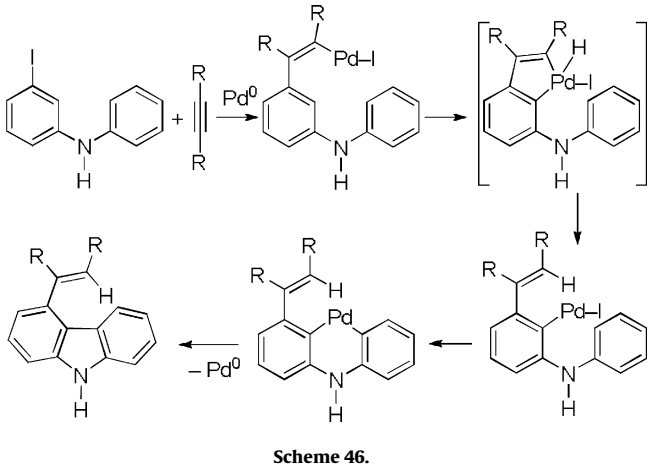
Scheme 44.

C–H, if there is time to equilibrate the biphenylyl-bonded Pd intermediate before reaction with a suitable C–C bond forming partner as in the cases of Heck and Suzuki reactions. Appropriate conditions to favor partial or total equilibration of the biphenylyl-bonded Pd intermediates have therefore to be chosen. For example if 2-iodo-4′-methylbiphenyl (Scheme 44) is subjected to a Suzuki reaction with phenylboronic acid the main product derives from the unrearranged intermediate. If however, the base needed for the activation of the phenyboronic acid is buffered using for example cesium pivalate and pivalic acid in equimolecular amount and phenylboronic acid is replaced by its *p*-carbomethoxy derivative a 51:49 mixture of the two products (78% overall yield) is obtained. According to the authors the preferred pathway implies a Pd(II) rather than a Pd(IV) intermediate (Scheme 45). As previously mentioned an electrophilic attack on the arene is not consistent with the acidity-dependent selectivity.

Larock has reported several reactions where he takes advantage of the migration process, for example the synthesis of 4-phenylfluorene [135] from 2-(3′-benzyl)phenyl iodobenzene and that of vinylcarbazoles [136] from *N*-(3-iodophenyl)anilines and alkynes. Vinylcarbazole formation has been proposed to proceed according to the pathway shown in Scheme 46. The vinylpalladium intermediate forms by oxidative addition of the aryl iodide and subsequent alkyne insertion. Cyclopalladation via selective *ortho* C–H bond activation is then followed by cleavage of the vinyl-metal bond to afford the arylpalladium species. The result is a 1,4 migration of Pd which is now in appropriate position for intramolecular ring closure through activation of a second aromatic C–H bond leading to carbazole and Pd(0). A possible involvement of a Pd(IV) species in the hydrogen transfer from the aromatic to the vinyl moiety has been proposed.



Scheme 45.



Scheme 46.

6. General considerations on the mechanism of arene C–H arylation

We have seen specific mechanistic aspects of the various types of arene C–H arylation. Common problems refer to the mechanisms of C–H activation and C–C coupling.

A study by Milstein on arene C–H activation has pointed out the importance of arene-bonded heteroatoms (Cl, OMe) in directing C–H activation towards the *o*-position [137].

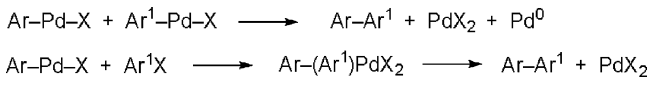
The traditional elctrophilic substitution mechanism seems to be operative in many cases. The metallation-deprotonation mechanism proposed by Echavarren and further confirmed by Fagnou appears to be valid for deactivated arenes and heteroarenes and possibly also in general [19,21a,22].

As to the aryl–aryl coupling process following arene C–H activation both transmetallation [138] and oxidative addition to give Pd(IV) have been postulated (Scheme 47) [109b].

Theoretical calculations conducted by Cárdenas and Echavarren have suggested that the latter process is not likely to occur [139]. Another recent paper by Grushin and Marshall also points to the inability of Pd(II) to undergo oxidative addition of unactivated aryl halides [140]. In fact under the reaction conditions Pd(II) is often reduced to Pd(0), which can undergo oxidative addition of an aryl halide to form an arylpalladium halide complex able to transmetallate.

In this connection a recent study by Dedieu should be considered [141]. Pd migration from aryl to aryl, likely involving palladacycle formation [133,134], may be favored by oxidative addition of an acid to the palladacycle, thus forming Pd(IV), if migration is 1,3 and through Pd(II)-catalyzed C–H activation-assisted by proton abstraction, if migration is 1,5 or 1,6; however, these pathways can compete in the case of 1,4 migration. The results indicate that very subtle effects can influence the energy of the transition state. In particular in the reaction of aryl halides in the presence of Pd and norbornene, initially involving the formation of a palladacycle by electrophilic activation of an unactivated arene C–H, the final coupling could well involve a Pd(IV) intermediate particularly under the multistep catalytic conditions adopted.

As to the state of the "true palladium" catalyst undergoing oxidative addition and insertion, in most cases nanoparticles are formed, that may be in equilibrium with momeric or dimeric form of ligandless Pd complexes [142–145]. Evidence for low ligated Pd–L as



Scheme 47.

the most active species undergoing oxidative addition has been provided by Amatore and Jutand [146].

7. Conclusions

Research in the area of aryl–aryl coupling reactions continues to grow exponentially, spurred by the importance of practical applications particularly in the pharmaceutical field, and the synthetic and mechanistic challenges.

Arene and heteroarene substrates have been arylated selectively through C–H activation reactions directed by chelation or by heteroatoms or by metallacycle formation. Research on catalytic systems hinges on design of homogeneous species on the one hand and of nanoparticles on the other as catalysts. This is a typical interdisciplinary area which will prove to become more and more fertile.

Acknowledgements

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