

Catalytic and stoichiometric C–C bond formation employing palladium compounds with nitrogen ligands

Cornelis J. Elsevier *

*Institute of Molecular Chemistry, Universiteit van Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands*

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Abstract

Carbon–carbon bond formation reactions catalyzed by palladium compounds containing bidentate nitrogen ligands is treated, with a focus on rigid ligands such as the bis(imino)acenaphthenes (bian) and bis(imino)phenanthrenes (bip), and ligands with larger bite-angles such as diazafluorenes and derivatives thereof. The emphasis is on recent work in this area by the author, but reference is made to relevant early and recent studies by others.

* Tel.: +31-20-525-6454; fax: +31-20-525-6456.

E-mail address: else4@anorg.chem.uva.nl (C.J. Elsevier)

After introducing the topic and the specific nitrogen ligands involved, several stoichiometric and catalytic C–C coupling protocols are treated. These involve intermediate palladium compounds in zero- di- and tetravalent oxidation states, which have been isolated and identified. Similarities and differences between catalysis by palladium compounds containing bidentate nitrogen ligands and systems containing mono- or bidentate phosphine ligands have been exemplified. © 1999 Elsevier Science S.A. All rights reserved.

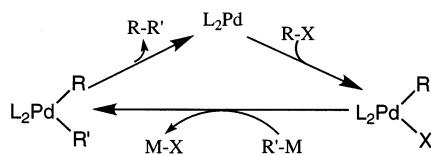
Keywords: Palladium; C–C coupling; Nitrogen ligands; Catalysis; Selective synthesis; Tetravalent palladium

1. Introduction

Transition metal catalyzed C–C coupling protocols belong to a group of very important reactions and many examples are known, especially palladium-catalyzed varieties, e.g. Heck, and cross-coupling reactions are very prominent tools for the synthetic chemist. The palladium catalyzed cross coupling methodologies constitute the most versatile protocols leading to new carbon–carbon bonds, since a variety of organic and organometallic substrates can be used. The coupling generally consists of a joining of an electropositive carbon fragment, derived from an organic halide, acetate or triflate, and an electronegative carbon fragment derived from an organometallic reagent, like organomagnesium, -zinc, -tin, -boron and -fluorosilicate compounds. The basic, generally accepted, mechanism for this type of cross coupling reaction consists of a sequence of oxidative addition, transmetalation and reductive elimination (Scheme 1, [1]).

For these catalytic reactions, mainly palladium and nickel complexes have been used. For Pd-catalyzed coupling reactions, P-ligands have commonly been employed; other types of ligands, such as N-ligands, have received relatively little attention up to the mid 1990s. When we started our investigations on C–C coupling mediated by Pd complexes carrying bidentate nitrogen ligands in 1987, only very few catalytic Pd(NN)-induced C–C couplings were known. The few examples included those by the groups of R. Süstmann [2] and B.M. Trost [3]. Stoichiometric reactions were known from studies by the groups of A. Canty [4], M. Catellani [5], B. Åkermark [6] and others.

Our interest in the C–C coupling behavior of systems containing ligands other than those based on phosphorus donors, stems from the knowledge that the various reactions taking place in the mechanism of C–C coupling shown in Scheme 1,



Scheme 1.

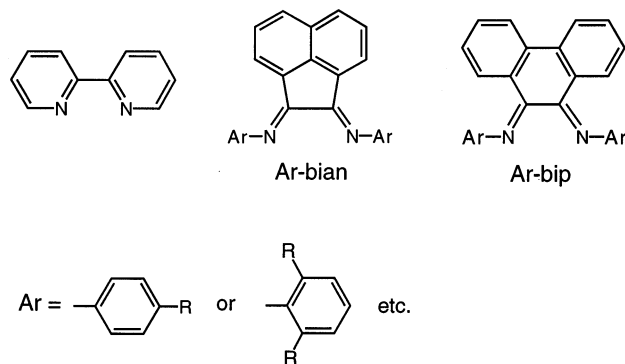


Fig. 1.

especially oxidative addition [7] and reductive elimination [8,9], largely depend on the steric and electronic properties of the ligands coordinated to the metal center. Hence, appreciable effects on the rates and selectivities of a number of such reactions may a priori be expected.

2. Nitrogen ligands

We have developed rigid bidentate N-ligands, particularly the so-called Ar-bian and Ar-bip (Fig. 1), which have been designed to combine suitable donor and acceptor properties, and thus should be amenable to the synthesis and reactions of zero-, as well as di- and tetravalent organopalladium species. At the time we started, previous studies had mainly been focused on open-chain diimines, e.g. [10–12]. The Ph-bian compound had been synthesized before [13].

The choice of Ar-bian and Ar-bip ligands was based on both electronic and steric arguments. Firstly, unlike phosphine ligands, such compounds combine good σ -donor with π -acceptor properties, are thus capable of stabilizing both higher and lower oxidation states. These features will be of imminent importance in an alternating sequence of oxidative addition and reductive elimination. Secondly, the rigidity of the acenaphthene backbone forces the imine N-atoms to remain in a fixed *cis* orientation, favoring a chelating coordination to metal complexes. This chelating coordination leads to complexes with *cis* geometry of the type $\text{Pd}(\text{R})(\text{R}')(\text{Ar-bian})$, which have both organic groups in a *cis* orientation, thus facilitating reductive coupling from this type of complexes. When comparing to *trans*- $\text{M}(\text{R})(\text{R}')(\text{PPh}_3)_2$ ($\text{M} = \text{Ni}, \text{Pd}$), the reductive elimination of $\text{R-R}'$ from such compounds cannot take place directly. Generally, isomerization is necessary, or reductive elimination occurs from a three- or five-coordinate intermediate [14]. Furthermore, the use of Ar-bian ligands in catalytic systems is advantageous for mechanistic studies, because the steric properties of the ligand, and the steric crowding around the palladium center to which it is coordinated, can be controlled

and modified by variation of the aromatic substituent on the imine-N atoms and the influence of these substituents on catalytic and stoichiometric reactions studied.

A large number of such ligands have indeed been obtained and have subsequently been employed in a number of stoichiometric and catalytic reactions. To date, we have found that the Pd(Ar-bian) complexes homogeneously catalyze reactions such as C–C, C–H, C–N and C–X coupling. Some of our most important findings have been highlighted below.

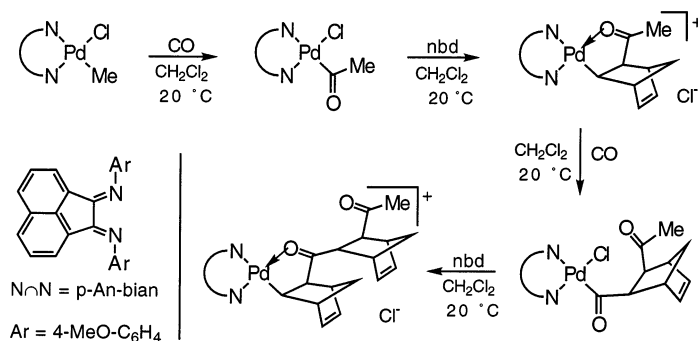
3. Carbon–carbon coupling reactions

3.1. General

During our initial work, a number of papers on catalytic C–C coupling reactions mediated by Pd(NN) compounds have appeared [15,16]. Later on, concomitant with and following several of our publications on this work dealing with the ligand design and synthesis [17,18], the C–C coupling [17,19,20] and alternating CO/alkene insertion reactions [21], many more have appeared. Recent examples of the very successful application of these [17,18] and similar [10–12] diazadiene ligands include the Pd- and Ni-catalyzed polymerization of olefins [22]. Furthermore, applications of Pd(NN) compounds have been achieved in the Heck reaction [23] and (catalytic) co-polymerization (see below).

3.2. Alternating CO/alkene insertions

One of the particularly interesting reactions we have studied concerns model reactions of CO/alkene co-polymerization reactions [21,24–27]. In this case the Pd(Ar-bian), particularly the Pd(4-methoxyphenyl) derivative, complexes were successfully employed in mechanistic studies of the stepwise alternating insertion of norbornadiene and carbon monoxide [21,27]. By doing so, it has been possible to execute successive insertions of CO and alkenes into Pd–alkyl and Pd–acyl bonds,



Scheme 2.

respectively (Scheme 2). Hence, it has been possible for the first time to follow a living copolymerization by stepwise reactions involving Pd(R)X(Ar-bian) compounds and to isolate several consecutive Pd-alkyl and Pd-acyl compounds. This type of reaction employing Pd(NN) compounds has received considerable attention by other teams, e.g. [28–31].

3.3. Palladium(IV) compounds

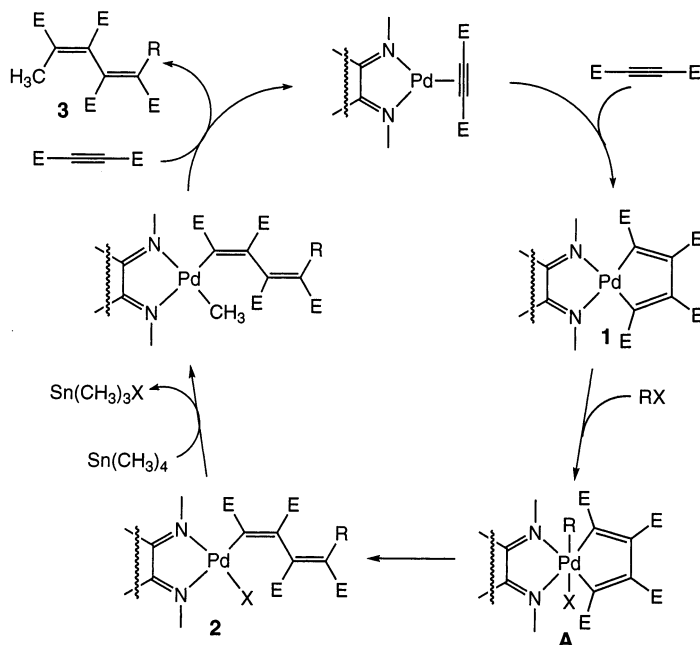
The involvement of hydrocarbylpalladium(IV) compounds in C–C bond formation has been proposed earlier [32], but their study has been facilitated only relatively recently due to the pioneering work of A. Canty c.s. [4,33]. Later studies have focused both on the synthesis of tris(hydrocarbyl)palladium(IV) compounds as well as mechanistic studies of C–C bond formation by elimination of hydrocarbons from such high-valent Pd species [4,34–36].

Ar-bian is able to stabilize organopalladium(IV) compounds in solution very well, just as and sometimes better than other bidentate N-ligands [4,13]. However, the *N*-aryl groups of Ar-bian ligands are positioned more or less perpendicular to the coordination plane in many of their complexes, thus bulky groups at the *o,o'*-positions of the *N*-aryl groups effectively screen off the space perpendicular to the coordination plane [37–39]. Hence, the relative stability of organoPd(II)(Ar-bian) vs. organoPd(IV)(Ar-bian) compounds may depend on whether or not substituents are present on the *N*-Ar groups; bulky substituents at the *o,o'*-positions render the Pd(II) center less accessible (e.g. for reagents in oxidative addition reactions [20]). Conversely, reductive eliminations from Pd(IV) to Pd(II) compounds may be faster since the steric strain in the 6-coordinate Pd(IV) compound will be relieved upon reductive elimination. On the other hand, proof has been obtained for the dissociation of one of the nitrogen donor atoms of rigid bidentate N-ligands in several cases [40,41], although this seems to be restricted mainly to zero- and divalent palladium species, the latter in particular in competition with η^3 -coordination of an allyl group [42].

3.4. Catalytic C–C bond formation involving Pd(IV)

We have recently shown [43,44] that Ar-bian, Ar-bip, bpy and similar bidentate nitrogen ligands are able to stabilize organo-Pd compounds of all common oxidation states within one catalytic cycle; they may be employed in catalytic reactions where Pd(0), Pd(II) as well as Pd(IV) occur along the reaction coordinate. This is an example of the development of a catalytic reaction from knowledge obtained from stoichiometric reactions which have been studied earlier (see Section 3.5). Based on this protocol, we have reported a new Pd-catalyzed three-component synthesis of conjugated dienes by coupling of alkynes with an organic halide and tetramethyltin.

The catalytic stereospecific synthesis of conjugated dienes (*Z,Z*)-**3** was achieved by adding **1** (1 mol%, or Pd(dba)_2 and an equimolar amount of Ar-bian or Ph-bip) as a precatalyst to a mixture of (2:1:1) dimethyl butynedioate, te-



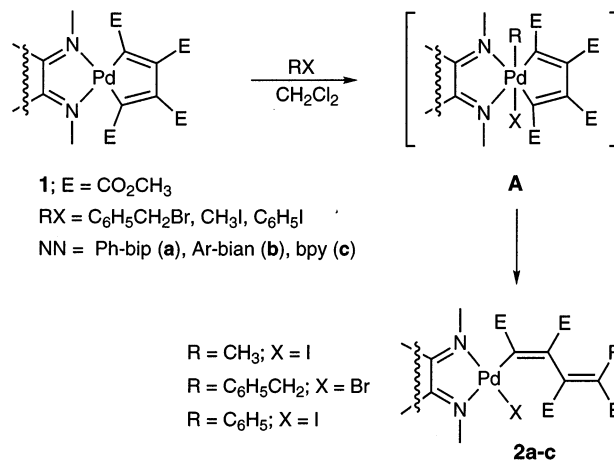
Scheme 3.

trimethyltin and an organic halide such as benzyl bromide, methyl iodide or iodobenzene in DMF at 65°C (Scheme 3, [37,38]). The best results were obtained when employing Pd(Ar-bian) compounds as the catalyst. Importantly, no direct cross-coupling reactions between the organic halide and tetramethyltin took place. Mechanistic details have been elucidated, revealing stereospecific oxidative addition–reductive elimination sequences at carbopalladacyclic compounds and that, sequentially, Pd(0), Pd(II) and Pd(IV) species are involved as intermediates (Scheme 3). The observation that three oxidation states of palladium are involved in the catalytic cycle merits further attention, especially in view of the current interest in catalytic reactions involving palladium in high oxidation states. Importantly, palladium(phosphine) species exhibit no catalytic activity whatsoever under the conditions described.

Others have made very important contributions to this field and have also recently shown the probable involvement of Pd(IV) intermediates in catalytic C–C bond formation reactions of various kinds [45,46]. Catalysis possibly involving high-valent palladium(phosphine) compounds have been the subject of debate but fall outside the scope of this paper [47].

3.5. Stoichiometric reactions involving Pd(IV) and Pd(II)

Prior to finding the above mentioned catalytic application, we have found that palladacyclic compounds **1** react with one equivalent of an organic halide (e.g.



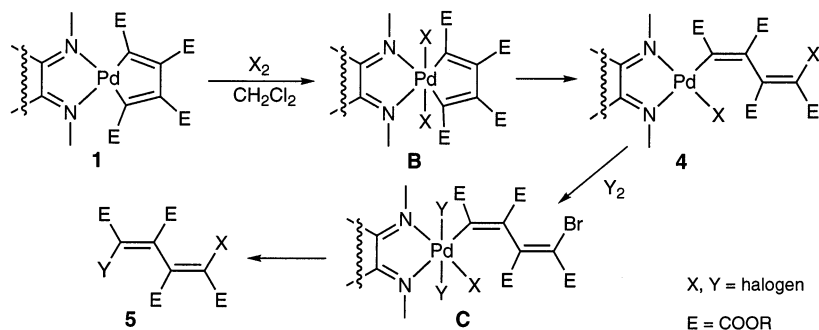
Scheme 4.

benzyl bromide, methyl iodide, iodobenzene) in dichloromethane at 20°C to give **2**. This reaction involves a sequence of oxidative addition and reductive elimination reactions, proceeding via triorganopalladium(IV) species **A** (Scheme 4).

Reaction of isolated **2** with tetramethyltin in DMF at 60–85°C lead to selective formation of 2,5-difunctional-2,4-hexadienoates **3**. In view of these findings and since the formation of palladacycles **1** from $[Pd(dba)_2]$ and electron-poor alkynes [48] is much faster than direct oxidative addition of benzyl bromide to $Pd(0)$, whereas the insertion of a third molecule of acetylene in **1** is slow compared to the reaction of the organic halide with **1** to give **2**, we anticipated a catalytic procedure for the synthesis of dienes **3**, which has indeed been obtained (Scheme 3). Recently, several reports have appeared about the synthesis of and stoichiometric reductive eliminations from triorganopalladium(IV) compounds [33,34,36,45,46].

3.6. Stoichiometric C–X coupling

This paragraph concerns C–C and C-halogen bond formation and has been included since it contains important mechanistic information concerning the catalytic C–C coupling described above. Stoichiometric reaction of **1** with molecular halogens in dichloromethane at 20°C afforded stereoselectively (2*E*,4*E*)-2,5-dihalogeno-2,4-hexadienoates **5** (Scheme 5). Intermediate **B**, a diorgano-Pd(IV) dihalide, is formed instantaneously and quantitatively in CD_2Cl_2 as was demonstrated by in situ 1H -NMR at 200 K [43]. From successive reactions of **1** and **4** with different halogens it was proved that organopalladium(IV) trihalide species **C** are



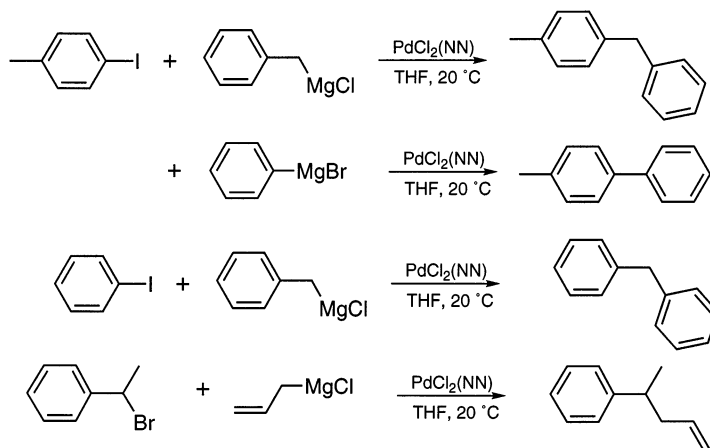
Scheme 5.

involved and that chemo- and stereospecific reductive eliminations from **C** involving one of the apical halogens and the dienyl moiety occur: e.g. no elimination of dibromodienes was observed from the reaction of **4** (X = Br) with ICl [44]. Importantly, these stoichiometric reactions of alkynes to give dihalogenodienes **5** could not be effected with palladium(phosphine) analogues of **1** or **4**, nor any other Pd–phosphine compound [43,44].

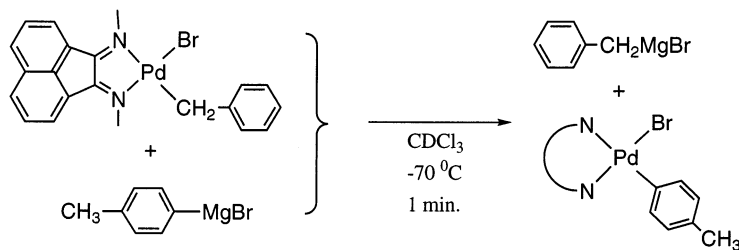
3.7. Cross-coupling involving rigid bidentate *N*-ligands

On previous occasions [17,19,20] we have studied the Pd(NN)-catalyzed cross-coupling (Scheme 6) and homo-coupling reactions and specifically the mechanism of the homo-coupling reaction in a number of cases [20,47].

The Pd(Ar–bian) and similar Pd(NN) complexes are good catalysts for the cross-coupling of organic halides with organomagnesium, -zinc and -tin reagents



Scheme 6.



Scheme 7.

and are complementary to the commonly employed, often in situ formed, palladium(phosphine) compounds. These reactions proceed via diorganopalladium(II)(Ar–bian) compounds. Organopalladium(IV) compounds are not involved. It has been shown that the concurring formation of homo-coupled products in a number of these reactions is due to exchange of the organic groups in the initial organopalladium and organomagnesium or -zinc compounds (Scheme 7, [19,20]).

We have extended these studies by employing a number of bidentate nitrogen ligands (Fig. 2) with different properties, such as their bite-angles, acceptor properties and basicities.

In several simple C–C coupling reactions (Scheme 6), the yields and selectivities for cross-coupled products appeared to be similar for most of the ligands in Fig. 2 and usually are comparable to or somewhat better than those catalyzed by Pd compounds containing phosphine ligands such as triphenylphosphine and bis(diphenylphosphino)ethane, e.g. the coupling of allylmagnesium chloride with 1-phenylethyl bromide (Scheme 8, Table 1, [47]).

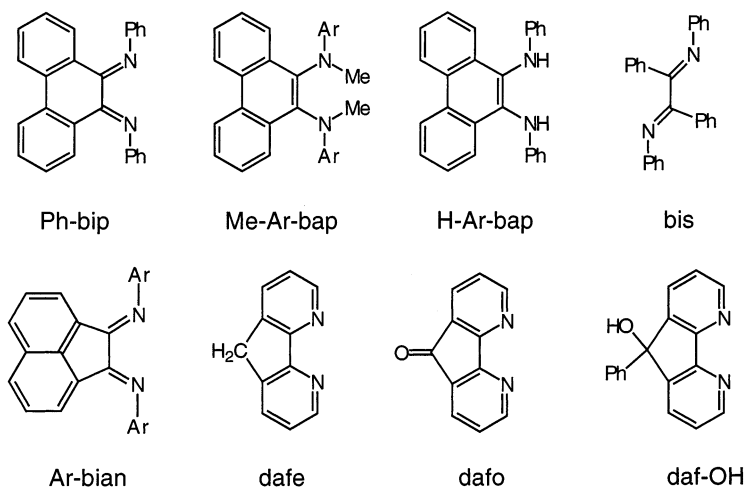
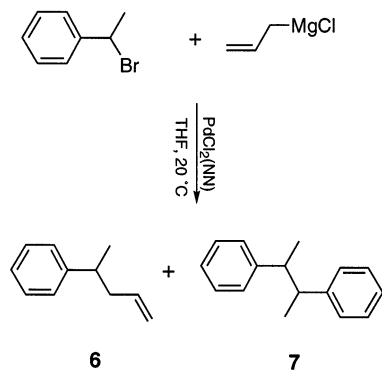


Fig. 2.



Scheme 8.

Table 1

Ligand	Ar-bian	Ph-bip	Me-Ar-bap	bis	PPh ₃	dppe
% Cross (6)	85	82	82	81	80	60
% Homo (7)	15	18	18	19	20	40
% Conversion	88	57	80	72	64	99

Only in the case of coupling between *p*-tolyl iodide and phenyl Grignard, palladium(phosphine) compounds are superior to most of the palladium compounds containing nitrogen ligands. Palladium(phosphine) compounds give results similar to the Pd compounds containing daf or daf-OH ligands (Fig. 2). When employing Pd compounds with N-ligands (1 mol% relative to the substrates), the amount of homo-coupling products is usually lower than the same reactions with PPh₃ or dppe as the ligands. For coupling of aryl bromides (as opposed to iodides), phosphine ligands give better results in terms of conversion as well as selectivity [17,19,20,47].

3.8. Effect of bite-angle and rigidity

We have recently explored the influence of the bite-angle of the bidentate N-ligands on the reactivity and selectivity in Pd-catalyzed C–C bond formation to some extent [47,49]. The 4,5-diazafluorene (dafa), 4,5-diazafluoren-9-one (dafo) and 4,5-diazafluoren-9-ol (daf-OH) ligands (Fig. 2) have a substantially larger bite-angle (about 82°) as compared to 2,2'-bipyridyl and Ar-bian (77°) (Fig. 3).

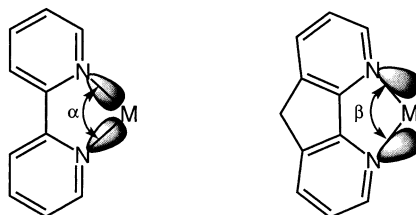
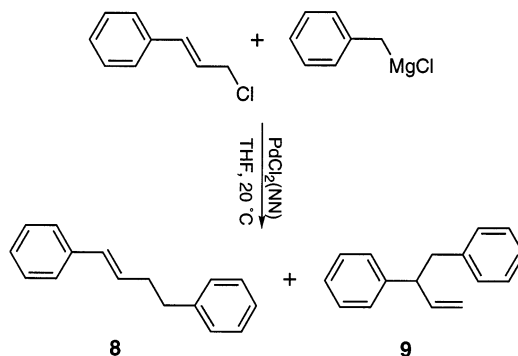


Fig. 3.



Scheme 9.

The specific features of the dafo and dafé ligands have enabled the isolation of divalent and zerovalent palladium compounds containing two N-ligands which are each coordinated via one N-atom or dimetallic species containing one bridging N-ligand [41,42]. The use of such compounds appeared to have a distinct influence on the product distribution in some C–C coupling reactions, which could in several cases be traced to the dimeric or bimetallic nature of the catalytic species involved.

Especially in the reaction of cinnamylchloride with benzyl Grignard (Scheme 9, Table 2), a pronounced influence of the ligand has been noted. The regioselectivity of the allylic substitution when using Pd(NN) compounds as the catalyst is different from reactions catalyzed by Pd(phosphine) species, as has previously been observed for other allylic substitution reactions [6]. Not only is the selectivity for substitution at the less substituted allylic carbon much higher in cases employing Pd(NN) compounds as compared to Pd(phosphine) compounds, also the amount of homo-coupled products is appreciably lower. For the diazafluorene type of ligands, even complete regioselectivity is reached, with concomitant formation of only 5% of the homo-coupled product 1,2-diphenylethane (which is in part already present in the Grignard reagent). The high regioselectivity is attributed to the structure of the intermediate, where, as could be inferred from X-ray studies of

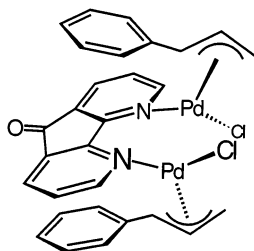


Fig. 4.

Table 2

Ligand	bip	Me–Ar–bap	bis	daf–OH	PPh ₃	dppe
% Cross (8)	65	67	74	95	44	38
% Cross (9)	5	7	4	0	25	21
% Homo (Bz ₂)	10	11	10	5	13	15
% Homo (Ph ₂ hex)	20	15	12	0	18	26
% Conversion	98	98	89	91	66	83

[Pd(PhCHCHCH₂)Cl]₂(dafo) and [Pd(PhCHCHCH₂)Cl]₂(dafe), the aryl rings of the daf/o ligand and the phenyl groups of the cinnamyl moiety are stacking (Fig. 4). As a consequence, the remote 3-position of the allylic moiety is better accessible for nucleophiles than the 1-position, either via direct attack or via substitution of chloride by the benzyl fragment [47].

4. Conclusion

Bidentate nitrogen ligands, especially the Ar–bian, Ar–bip and daf/o ligands, are effective ligands for the stabilization of palladium in all common oxidation states, as exemplified by the isolation of a number of compounds and their involvement as ancillary ligands in several homogeneous palladium-catalyzed reactions. In many cases, the performance of systems which contain Ar–bian is superior to those involving other (more common) nitrogen ligands. Several C–C coupling reactions are catalyzed by palladium compounds containing nitrogen ligands as the stabilizing and activating entities, but not by palladium compounds containing phosphine ligands. This complementarity, especially the effective stabilization of the tetravalent oxidation state of palladium, may lead to the further proliferation of nitrogen ligands in palladium mediated organic synthesis and catalysis.

Acknowledgements

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