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Historical note

A genealogy of Pd-catalyzed cross-coupling

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Abstract

This paper describes (a) a very brief history leading to the birth of the Pd-catalyzed cross-coupling, (b) its birth in the mid-1970s, (c) the development of the Pd-catalyzed cross-coupling with organometals containing Zn, Al, Zr, and Mg (the 'first-generation' Pd-catalyzed cross-coupling) in the 1970s, (d) seeding of the Pd-catalyzed cross-coupling with organometals containing Sn, B, and Si (the 'second-generation' Pd-catalyzed cross-coupling) in the late-1970s, and (e) further developments in the author's group in the 1980s. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pd-catalyzed cross-coupling; Organometals containing Zn, Al, Zr, and Mg; Hydrometallation–cross-coupling tandem; Carboalumination–cross-coupling tandem; Pd–Zn double metal catalysis

1. Introduction

> '... Nothing comes from nothing. Nothing ever would...'

As the author tries to trace back the history of any scientific development, this line of a song in a musical, Sound of Music, invariably crosses his mind. The history or the origin of the Pd-catalyzed cross-coupling is certainly no exception. As detailed below, the birth of the first generation of the Pd-catalyzed cross-coupling in the mid-1970s was almost certainly not a sudden, isolated event. Many indications suggest that it was even multi-original and multi-national and was conceived independently and simultaneously by at least a few to several chemists most probably influenced by various different preceding chemical developments. It is striking that, behind a widely recognized name, there is usually one or more hidden names of those who made seminal, pioneering contributions but have remained unrecognized or altogether forgotten. In most of the significant scientific developments, there are usually at least two important individuals: one who discovers something new and another who recognizes its potential significance and develops it. The latter usually receives major credits, but the former should be equally recognized and rewarded, because he/she truly deserves it.

Having set up a nearly impossible stage for the assigned task, the author shall nevertheless try to present the origin of the Pd-catalyzed cross-coupling as factually and objectively as possible. The author is well aware that this paper or any others of this nature will never meet with every chemist's approval, but he is hopeful that it will help straighten out the seemingly much distorted notion currently held by the chemical community.

In this paper, cross-coupling is somewhat arbitrarily defined by the equation shown in Scheme 1, where R^1 and R^2 are C groups and X is a halogen atom or a related heteroatom leaving group. Metals (M) are defined as all elements except H, C, and Groups 15–18 elements. So, there are currently about 85 metals. There are always some gray areas associated with any definitions. In this case, distinction between cross-coupling and homo-coupling is one such aspect. Those reactions that give mostly statistical or random mixtures of R^1R^2, R^1R^1, and R^2R^2 should probably be excluded from cross-coupling. On the other hand, any cross-coupling reactions are, in principle, applicable to the

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$$R^1M + R^2X \rightarrow R^1R^2 + MX$$

Scheme 1. Cross-coupling. Its definition

synthesis of homo-coupled dimers. The Heck reaction [1], which does not involve organometals (R^1M) as substrates, may not be considered as a cross-coupling reaction, but its alkyne version [2], especially the Sonogashira reaction [3] which involves the use of a catalytic amount of Cu(I) salts, is usually considered as a cross-coupling reaction. The Tsuji–Trost allylation [4] represents yet another gray area. The reaction is usually not considered as an example of cross-coupling probably because metal enolates are usually not considered as bona fide organometals. And yet, the Reformatsky reagents are often represented as $XZnCH_2COOR$ and considered as organometals. Another reason might be that its mechanism involving a nucleophilic attack on π-allylpalladium derivatives by enolates is distinct from the well-accepted Pd-catalyzed cross-coupling mechanism. It should be agreed, however, that cross-coupling as defined by Scheme 1 does not imply any mechanism beyond the starting material–product relationship. Finally, the definition of cross-coupling has recently been substantially expanded so as to include H, heteroatoms, e.g. N and O, and even metals, e.g. B, Si, Sn, and transition metals, as R^1 of R^1M. In this paper, none of these heteroatom versions is considered.

2. Cross-coupling before the advent of the Pd-catalyzed cross-coupling

2.1. Earlier history

Cross-coupling, as defined above, is one of the most straightforward and general methods for the formation of carbon–carbon bonds. And yet, its development had been surprisingly sluggish until a few decades ago. Since the early developments of cross-coupling are to be discussed in some of the preceding sections, no rigorous discussion of such topics is intended here. Suffice it to state that before the 1960s the scope of cross-coupling as defined in Scheme 1 was largely limited to those involving Mg and Li. In general, organometals containing these metals undergo synthetically useful cross-coupling only with certain relatively unhindered alkyl halides, such as those containing methyl, primary alkyl, allyl, benzyl, and so on. Unsaturated organic halides containing C_{sp2}–X and C_{sp}–X bonds do not generally undergo cross-coupling with Grignard reagents and organolithiums [5]. Even their reactions with alkyl halides are subject to various side reactions, such as non-selective metal–halogen exchange and α and β eliminations. Yet another general difficulty associated with organometals containing Mg and Li is their generally low chemoselectivity. At this point, it would be useful to note that there can be at least ten side reactions listed in Table 1 that can be associated with cross-coupling reactions. Highly satisfactory cross-coupling reactions are those that are generally applicable and are capable of selectively providing the desired products in high yields, while avoiding all or most of these side reactions.

Table 1
Side reactions in the cross-coupling reactions

Entry	Side reaction
1	Formation of R^1–R^1
2	Formation of R^2–R^2
3	Reduction of R^2X to give R^2H
4	α Elimination to give carbenoids
5	β Elimination to give alkenes
6	Stereoisomerization
7	Regioisomerization
8	Reactions of functional substituents
9	Other undesirable reactions of substrates
10	Undesirable reactions of catalysts, ligands, solvents, added reagents, adventitious chemicals, etc

The development of the organocopper-based method [6] especially in the 1960s solved many of the difficulties associated with Mg and Li. Even so, a number of other problems remained unsolved.

2.2. Transition metal-catalyzed cross-coupling before the advent of the Ni-catalyzed cross-coupling

The early history of the transition metal-catalyzed cross-coupling can be mostly traced back to the Kharasch reaction [7] investigated and reported in the 1950s. Various transition metal salts were added as catalysts for the reaction of Grignard reagents with organic halides, but Pd may not have been employed. Various catalytic effects were observed, but the Kharasch reaction was generally not well suited for cross-coupling with a notable exception of the Cu-catalyzed version developed by Kochi and his coworkers [8]. The reaction of alkylmagnesium halides with alkyl electrophiles catalyzed by Li_2CuCl_4 known as the Kochi catalyst has become the method of choice for many cases of alkyl–alkyl coupling and some other related reactions.

It should be noted that, in the Kharasch and related reactions, no phosphine and other strong donor-type ligands appear to have been employed. This may have severely limited their synthetic scope in general. Moreover, there are few indications of the use of unsaturated organic electrophiles in the early investigations. For further details of this topic, the readers are referred to a paper by J. Kochi in this issue.

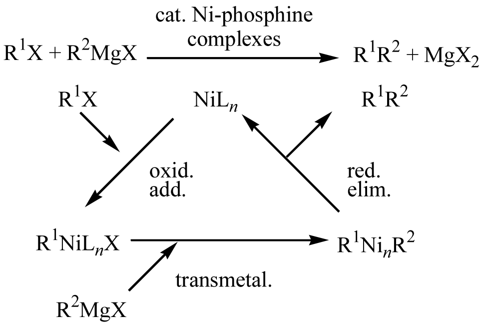
2.3. The Kumada–Tamao–Corriu Grignard cross-coupling catalyzed by Ni-phosphine and other Ni complexes

The discovery in 1972 [9] and subsequent systematic investigations [10] of the Ni-catalyzed cross-coupling reaction of Grignard reagents by Kumada, Tamao, and their associates represent in many respects the birth of the modern transition metal-catalyzed cross-coupling. First, the use of phosphine ligands made the catalysis by Ni a widely applicable and dependable synthetic methodology. Second, the widely adaptable mechanistic notion of a catalytic cycle consisting of (i) oxidative addition, (ii) transmetalation, and (iii) reductive elimination was explicitly presented and extensively exploited in a synthetically useful manner (Scheme 2). It should be noted that the reaction represents not only the beginning of a new era but also the culmination of many preceding contributions including studies of some Ni-promoted stoichiometric C–C bond formation reactions by Yamamoto et al. [11] and Semmelhack et al. [12]. It is gratifying that a rather limited but seminal, independent contribution by Corriu and Masse [13] has been widely recognized. Much less well recognized, however, is another seminal, if rudimentary, study of the Ni-catalyzed reaction of MeMgBr with allyl alcohols by Felkin and his coworkers [14].

3. The Pd-catalyzed cross-coupling

The discovery of the Pd-catalyzed cross-coupling was more subtle and evolutionary than that of the Ni-catalyzed cross-coupling. Explicitly or implicitly, the former must have been influenced by the latter.

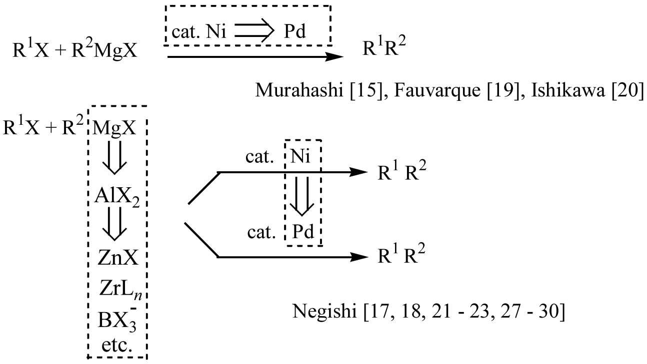
During the 1975–1976 period, several groups of workers including Murahashi and his coworkers [15], Cassar [16], Negishi and his coworkers [17,18], Fauvarque and Jutand [19], and Sekiya and Ishikawa [20] reported seemingly independent, if not simultaneous, studies of some Pd-catalyzed cross-coupling reactions. The alkyne version of the Heck reaction [2] and its variant using Cu(I) salts and Pd complexes as catalysts known as the Sonogashira reaction [3] were also reported during the same period. The evolutionary nature of some of these contributions is schematically indicated in Scheme 3. Most workers also adopted the three-step mechanism shown in Scheme 2 with due modifications. Survey of the literature on the Pd-catalyzed cross-coupling indicates that just a little more than two dozen papers on this topic were published during the 1975–1979 period [15–40].



Scheme 2. Ni-catalyzed Grignard cross-coupling and a three-step mechanism.

During the first 3 or 4 years, most of these ‘first-generation’ researchers in this area published just one or two papers each by using mostly Grignard reagents as organometals to devise what amounted to a Pd analogue of the Kumada–Tamao–Corriu reaction. Moreover, most of the products in these studies were those that could also be readily preparable by the Ni-catalyzed reaction. So, advantages of Pd catalysis were essentially unknown.

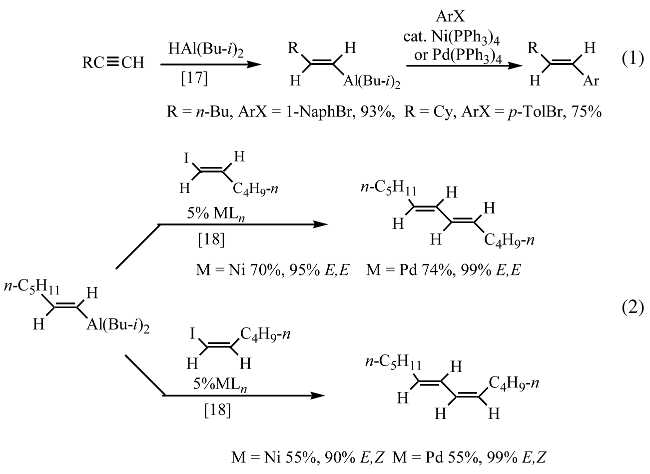
On the other hand, Negishi first replaced Mg in the Kumada–Tamao–Corriu reaction with Al to discover the Al–Ni combination [17,18]. Unfortunately, this protocol displayed deterioration of stereospecificity down to 90–95% in the conjugated diene synthesis [18]. By screening the other two members of the Ni triad, however, the Pd-catalyzed alkenylalane coupling providing a nearly 100% stereoselective method for the synthesis of conjugated *E*, *E* and *E*, *Z* dienes was discovered [18] (Scheme 4). These results permitted the following important generalizations. First, Mg in the Kumada–Tamao–Corriu reaction can be replaced with Al, indicating for the first time that other metals capable of participating in the putative transmetalation step in Scheme 2 might also serve as satisfactory metal countercations. Second, an explicit comparison of Ni and Pd was performed for the first time, and a distinct advantage of Pd over Ni was unequivocally demonstrated. Third, a hydrometalation–cross-coupling tandem process involving Pd or Ni catalysis was devised for the first time.



Scheme 3. Evolutionary discoveries and developments of the Pd-catalyzed cross-coupling.

These and subsequent studies have indicated that Ni is more prone to those side reactions listed as the items 6–9 in Table 1 than Pd, and the range of organic compounds that can be readily prepared with Pd catalysts is considerably wider than that with Ni catalysts. For example, alkyne-containing compounds, conjugated dienes, and nitro-substituted arenes are more satisfactorily synthesized by using Pd than Ni. In cases where Ni is satisfactory, however, Ni should probably be considered first, as it is significantly less expensive than Pd.

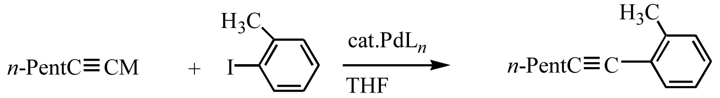
Difficulties were initially encountered in the attempted use of alkenylboron derivatives [17,18]. The favorable results observed with Al, however, prompted the author's group to conduct metal countercation screening with readily and widely available alkynylmetals [27]. As the results summarized in Table 2 indicate, Zn, B, and Sn were shown to be very satisfactory in providing the desired alkyne in high yields. Thus, those three metals that are currently most widely used were identified in this countercation survey conducted almost a quarter of a century ago. In terms of the date of publication, however, the use of Zn in the Pd-or Ni-catalyzed cross-coupling was first reported already in 1977 by Negishi et al. [21,23] and Fauvarque and Jutand [24]. Also reported in the same year was the first Pd-catalyzed C–C cross-coupling with organotins by Kosugi et al. [25,26]. So, the Pd-catalyzed cross-coupling reactions of both organotins [25–27] and organoborons [27] had in fact been seeded by Kosugi and Negishi before Stille and his coworkers [31,40] and Suzuki et al. [38,39] published their first papers on Pd-catalyzed cross-coupling with Sn and B, respectively (Scheme 5).



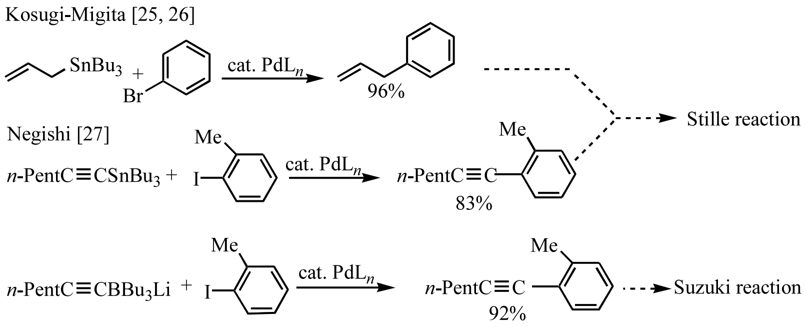
Scheme 4. Pd- or Ni-catalyzed cross-coupling with alkenylalanes.

The scope of the hydrometalation–cross-coupling tandem process was substantially expanded by (i) the discovery of the Pd- or Ni-catalyzed cross-coupling of alkenylzirconium derivatives during the 1977–1978 period [22,29,30] (Scheme 6) and (ii) the development of the carboalumination–cross-coupling tandem process first reported in 1978 [30]. The latter incorporated, for the first time, the generally applicable principle of 'double metal catalysis', i.e. acceleration of the Ni- or Pd-catalyzed cross-coupling by the addition of co-

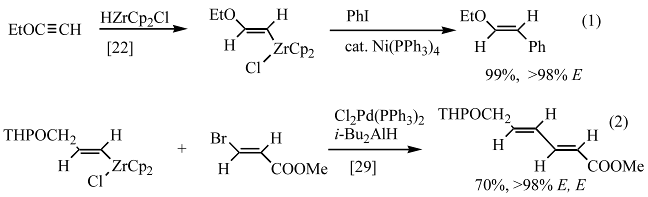
Table 2
Reaction of 1-heptynylmetals with *o*-tolyl iodide in the presence of $Cl_2Pd(PPh_3)_2$ and 2 DIBAH [27]



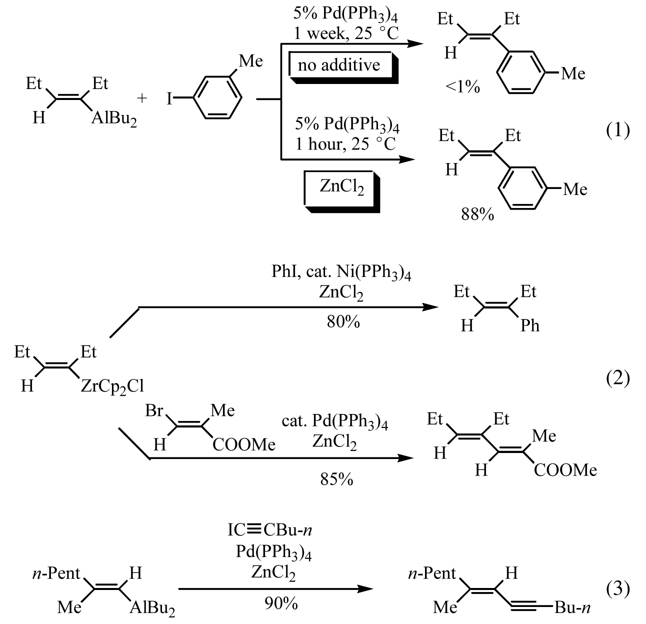
M	temp (°C)	time (h)	product yield (%)	starting material (%)
Li	25	1	trace	88
Li	25	24	3	80
MgBr	25	24	49	33
ZnCl	25	1	91	8
HgCl	25	1	trace	92
HgCl	reflux	6	trace	88
BBu_3Li	25	3	10	76
BBu_3Li	reflux	1	92	5
$Al(Bu\text{-}i)_2$	25	3	49	46
$AlBu_3Li$	25	3	4	80
$AlBu_3Li$	reflux	1	38	10
$SiMe_3$	reflux	1	trace	94
$SnBu_3$	25	1	75	14
$SnBu_3$	25	6	83	6
$ZrCp_2Cl$	25	1	0	91
$ZrCp_2Cl$	reflux	3	0	80



Scheme 5. Early examples of the Pd-catalyzed cross-coupling with organotin and organoboron compounds.



Scheme 6. Pd- or Ni-catalyzed cross-coupling with alkenylzirconium derivatives.



Scheme 7. Pd–Zn- or Ni–Zn-cocatalyzed alkenylation with alkenylmetals containing Al or Zr [30].

catalysts, most effectively Zn salts [30] (Scheme 7). In fact, preformed alkenylzinc derivatives are generally the most reactive and satisfactory class of alkenylmetals [20,41]. These investigations summarized in Schemes 4, 6 and 7 not only provided probably the most general and satisfactory procedures for the stereoselective syntheses of dienes, enynes, and other related stereodefined and delicate organic compounds but also set the stage for related later developments with B [42], Sn [43], Cu [44], and others achieved mainly in the 1980s.

As useful and important as the above-discussed developments are, the most noteworthy and practically important progress made during the 1976–1978 period is, however, the discovery followed by the development of the Ni- or Pd-catalyzed organozinc cross-coupling [21,23,28,30]. More electronegative metals, such as B [42], Sn [43], and even Si [45], may prove to be highly satisfactory, perhaps even more so than Zn, for the synthesis of some robust compounds, such as biaryls, and polymers requiring purification of difunctional starting materials. Even so, Zn has nonetheless provided and should continue to provide the most satisfactory overall package combining (i) high reactivity, (ii) high stereo-, regio-, and chemoselectivities, (iii) widest scope and applicability, and (iv) relative absence of strongly negative features, such as serious toxicity problems.

It has been repeatedly noted that those metals that are more electropositive than Zn, such as Li, Na, and even Mg, generally display not only lower selectivities, especially chemoselectivity, and narrower synthetic scopes but also lower reactivity under catalytic conditions. It is not unreasonable to speculate that their high intrinsic reactivity leads to various forms of catalyst poisoning or inactivation, as experimentally demonstrated in some cases [46]. Despite all these unfavorable features, these electropositive metals, especially Mg, should be seriously considered first at least in those cases where they are used as the metal countercations in the precursors to other organometals containing Zn, B, Sn, and so on.

In summary, the Pd-catalyzed cross-coupling reactions involving Mg and three other metals of intermediate electronegativity, i.e. Zn, Al, Zr, were discovered and substantially developed during the 1975–1978 period. It may therefore, be reasonable to consider them as a quartet of the ‘first-generation’ Pd-catalyzed cross-coupling reactions. They are characterized by the use of relatively electropositive metals, and some of their salient features are discussed above.

The birth of the ‘second-generation’ Pd-catalyzed cross-coupling with more electronegative metals, i.e. B, Sn, and Si, was witnessed only a few years after that of the first-generation reactions, i.e. during the 1977–1978 period. However, their extensive developments were carried out mostly in the 1980s and later. Toxicity is indeed a serious factor limiting the use of Sn. On the other hand, the significance of highly electronegative and generally non-toxic B and Si appears to be increasing. Essentially all Main Group metals have been considered and screened. Among transition metals, Zr has so far been the only widely accepted metal mainly for the synthesis of alkenes. Although less well-developed and less widely accepted, the Pd-catalyzed cross-coupling of preformed organocoppers is promising and needs to be further investigated. A few other relatively inexpensive transition metals, such as Mn, may also turn out to be useful.

In the title of the ref. [27] published in 1978, this author raised a prophetic question: “Is Ni or Pd better than Cu?” Today, the following prophetic question may be somewhat playfully presented: “Will Zn and B dominate the Pd-catalyzed cross-coupling, with several others including Mg, Al, Zr, Si, Sn, and perhaps Cu playing significant supporting roles?”

4. Further developments in the author’s group in the 1980s

Although the foundation of the Pd-catalyzed cross-coupling was established in the 1970s, its extensive developments and synthetic applications have been performed mostly since 1980. These activities are, however, so extensive and diverse and their discussion is clearly beyond the scope of a paper like this. In the author’s group alone more than two dozen papers [46–71] were published in the 1980s. Significantly, most of these papers reported either the earliest or some of the earliest results on the respective topics, of which those listed below are synthetically useful and/or otherwise noteworthy:

1) Pd-catalyzed alkylation [47,54,68], silylmethylation [43], homoallylation [47,48,60], homopropargylation [47,48,60], homobenzylation [60] with the corresponding organometals containing Zn and Mg (since 1980). Hayashi and the author independently made oral presentations on this topic in 1979, and Hayashi’s paper was published in the same year [37]. However, the author’s first two papers on the topic were published a year later [47,48].
2) Pd-catalyzed aryl–allyl [49,52,64], alkenyl–allyl [49,51,52,63,65], benzyl–alkenyl [50], and alkenyl–benzyl [50] coupling reactions, where the first entry in the hyphenated term represents the carbon group in the corresponding organometallic reagent (since 1981). It should be noted that the Pd-catalyzed allylation of organometals was considered to be unfavorable as of 1980 [4a].
3) Pd-catalyzed allylation of ‘ordinary’ metal enolates containing B and Zn, where the ‘ordinary’ metal enolates are defined as those enolates that are not extra-stabilized, malonic esters and acetoacetic esters being some of the representative examples of the extra stabilized enolates. [55,57,59,65,66] (since 1982).‘Ordinary’ metal enolates were considered to be unsatisfactory substrates in the Tsuji–Trost reaction as of 1980 [4a].
4) Pd-catalyzed acylation of organozincs [61] (since 1983). This has been extensively applied to the synthesis of ketones.
5) Pd-catalyzed ‘pair-selective’ synthesis of conjugated diynes [62] (since 1984). Together with more recent developments in the author’s group [72,73], this method has provided a highly selective and superior route to conjugated diynes.
6) Strictly regioselective α-substitution of carbonyl compounds via Pd-catalyzed cross-coupling of α-haloenones and related derivatives (since 1987). A seminal contribution published in 1987 [70] led the way to later developments in the 1990s [74].
7) Mechanistic investigations of the Pd-catalyzed cross-coupling [67,69,71] including the first demonstrations of (i) catalyst poisoning with organolithiums [46] and (ii) the intermediacy of metal palladates [67], i.e. $LiClPd(PPh_3)_2$ and $Li_2Cl_2Pd(PPh_3)_2$, in some Pd-catalyzed cross-coupling reactions.

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