Palladacycles − An Old Organometallic Family Revisited: New, Simple, and Efficient Catalyst Precursors for Homogeneous Catalysis

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Dedicated to the memory of Professor John Osborn

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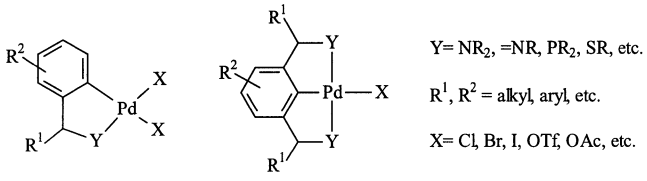
Nitrogen-, phosphorus-, and sulfur-containing palladacycles, typically containing four- or six-electron donor anionic metallated ligands, are emerging as a new family of organometallic catalyst precursors. These thermally and air-stable complexes are easy to handle and their synthesis is often straightforward. Palladacycles are now being successfully exploited in catalytic reactions ranging from classical hydrogenations to enantioselective aldol-type condensations. The main recent achievements pertaining to their use in homogeneous organometallic catalysis are outlined herein.

Introduction

Palladacycles are a popular and thoroughly investigated class of organopalladium compounds. The vast majority of these complexes possess anionic four-electron (bidentate) or six-electron (tridentate) donor ligands, with five-membered nitrogen-containing rings being the most common (Scheme 1).[1] Such systems have been known since the 1960s.[2]



Scheme 1. Examples of palladacycles

Their synthesis is facile and it is possible to modulate their electronic and steric properties simply by changing (i) the size of the metallacyclic ring (3−10 membered), (ii) the

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Michel Pfeffer was educated at the University of Strasbourg, where he obtained his Ph.D. in 1975 in the Laboratoire de Chimie de Coordination with Prof. Jean Dehand. He then spent one year with Prof. F. G. A. Stone at the University of Bristol as a postdoctoral student. Since 1973, he has held a position in the CNRS at the UniversitéLouis Pasteur in Strasbourg, where he became Directeur de recherche in 1985. His current research interests lie at the interface of inorganic, organometallic, and organic chemistry, with an emphasis on metal-mediated functionalization of C−H bonds through reactions aimed at producing new carbon−carbon or carbon−heteroatom bonds.

John Spencer obtained a B.Sc. (1st class, Hon.) at Sussex University in Chemistry with European Studies in 1990 before studying for a Ph.D. under the supervision of Michel Pfeffer, Strasbourg (1990−1994). After a postdoctoral stay with Antonio Togni at the ETH, Zurich, he returned to England where he first worked in the pharmaceutical industry (Xenova, Cerebrus). He then took up his current position at the Thrombosis Research Institute (London), where he is now a Senior Research Scientist. He is a co-author of over a dozen papers and patents and his research interests include organopalladium and organoboron chemistry, as well as asymmetric catalysis.

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nature of the metallated carbon atom (aliphatic, aromatic, vinylic, etc.), (iii) the type of donor group (N-, P-, S-, O-containing group, etc.) and its substituents (alkyl, aryl, etc.), or (iv) the nature of the X ligands (halide, triflate, or solvent, e.g. THF, H_2O). These factors determine whether the complex is dimeric, monomeric, neutral, or cationic. This flexibility confers a plethora of potential applications upon this class of compounds.

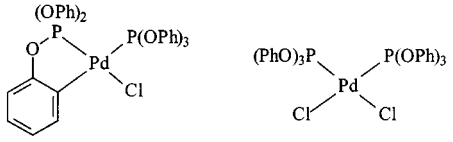
In the following applications, palladacycles can be further subdivided into two classes of compounds: one in which the Pd−C bond remains intact, i.e. the cyclopalladated unit is used as an ancillary ligand, and a second class where the palladated carbon atom is functionalized (mainly for organic synthesis). Indeed, these complexes have been used as intermediates for organic synthesis,[3] as new materials[4] (in liquid crystals, nonlinear optics, etc.), in bioorganometallic chemistry,[5] and, much more recently, they have undergone a renaissance as a result of their increasingly impressive applications in organometallic homogeneous catalysis.

The catalytic properties of cyclopalladated complexes were investigated more than a decade ago,[6] although previous reviews have tended to focus on the synthesis of palladacycles and their applications in mainly stoichiometric processes with scant progress being achieved in the area of catalytic applications. It is only recently that the true potential of palladacycles in organometallic catalysis has been recognized. There are two intriguing aspects regarding this last point: (i) the Pd−C bond in the majority of palladacycles is reactive towards a wide range of nucleophilic and electrophilic reagents exploited in catalysis, and (ii) the palladacycle can often be recovered unchanged following catalysis and can sometimes even be recycled. Mechanistic studies aimed at ascertaining the actual role of the palladium atom in these catalytic systems are a matter of intense current discussion since, besides the classical Pd^0/Pd^{II} catalytic cycles, several studies are now pointing to the involvement of Pd^{II}/Pd^{IV} cycles. However, no definitive argument in favour of one or other of these hypotheses has yet been presented.

Palladacycles are now emerging as a new family of catalyst precursors for a host of reactions. These derivatives easily fall into the current paradigm for homogeneous catalysis; they are often easily prepared in high yields through a C−H activation process, are often air- and moisture-stable, and, once catalytically active (usually above 100 °C), can attain high turnover numbers (TONs). Their applications in mainly Heck-type reactions were recently reviewed by Herrmann and co-workers;[7] this review covered complexes derived from the palladation of tris(*o*-tolylphosphane) developed in their laboratory. However, as already mentioned, palladacycles offer a much wider variety of catalytic applications and several new and efficient complexes based on different ligand backbones have since been reported. This brief overview will concentrate on recent examples involving the use of genuine, well-characterized palladacycles as catalyst precursors, in particular for catalytic C−C bond-forming reactions.

Hydrogenations

The use of palladacycles as catalyst precursors for hydrogenations represents one of the first applications of this class of compounds in catalysis. It was demonstrated that cyclopalladated triphenyl phosphite was effective in promoting the hydrogenation of C=C bonds, whereas its non-*ortho*-palladated analogue decomposed under the catalytic conditions and did not promote the reduction reaction (Scheme 2).[6]

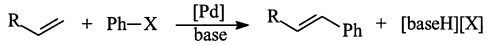


Scheme 2. Palladated and nonpalladated triphenyl phosphite ligands

The presence of a Pd−C bond in hydrogenation catalyst precursors, derived from the *ortho*-palladation of azobenzenes, hydrazobenzenes, or *N*,*N*-dimethylbenzylamine, was also found to be essential to effectively promote the selective reduction of nitroaromatic compounds, nitroalkenes, nitriles, alkynes, alkenes, and aromatic carbonyl compounds.[8] Surprisingly, however, despite the report of these very promising results, the use of palladacycles in reduction processes has not been further explored.

Heck Coupling Reactions

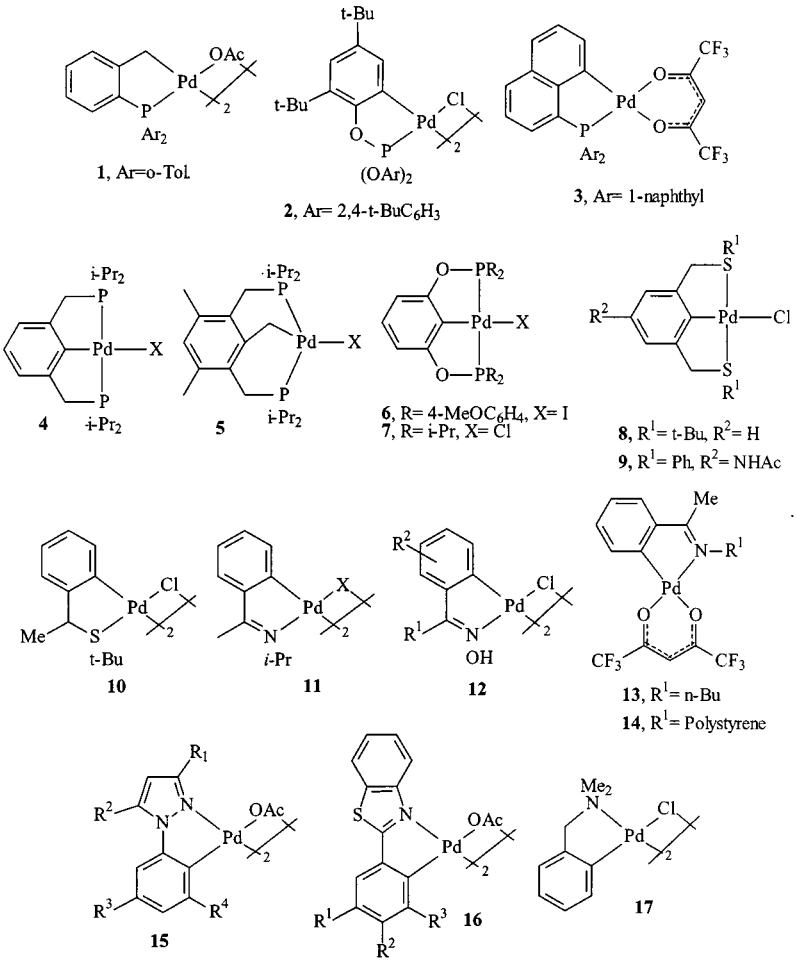
The arylation of C=C double bonds (Heck reaction)[9] is mediated by a variety of Pd^{II} and Pd^0 catalyst precursors (Scheme 3).



Scheme 3. Heck coupling reaction

In this context, phosphorus-,[7,10−21] nitrogen-,[22−27] and sulfur-containing[28−30] palladacycles are among the most active catalyst precursors for the promotion of such reactions reported to date (Scheme 4).

All of the palladacycles shown in Scheme 4 promote the Heck reaction of aryl iodides with acrylic esters (Table 1). In this reaction, the highest catalytic activity observed to date was achieved with the palladacycle **6** (Table 1, Entry 9). It is interesting to note that this palladacycle only promotes the Heck reaction between aryl iodides and acrylic esters. However, it should be pointed out that almost any Pd^{II} or Pd^0 derivative, irrespective of whether it is associated with stabilizing ligands, is capable of promoting Heck reactions involving aryl iodides or aryl bromides substituted with electron-withdrawing groups. In contrast, only a few palladacycles are active catalyst precursors for electron-rich aryl bromides (Table 1). Moreover, in the case of aryl chlorides, complexes **1**, **7**, **8**, and **11** were found to be the only active palladacycles (Entries 23−30, Table 1). In particular, **7** promotes the Heck reaction of electron-rich aryl chlorides, such as 4-chloroanisole (Entry 29, Table 1).[21]



Scheme 4. Palladacyclic catalyst precursors for the Heck reaction

It was recently demonstrated that cationic derivatives of binuclear conjugated palladacycles (Scheme 5) are also highly active catalyst precursors for the Heck reaction of iodobenzene with styrene or methyl acrylate.[31]

Palladacycles can also be involved in recyclable catalytic systems, e.g. by running the reaction of phosphapalladacycle **1**[32,33] in ionic liquids,[34] or by employing the polyethylene glycol bound sulfur-containing palladacycle **9**[28] or the polystyrene-bound imine-containing palladacycle (see later).[26] Moreover, trifluoroacetate-bridged derivatives of **1** have been shown to catalyse Heck reactions in supercritical carbon dioxide.[35,36]

Palladacycle **1** has also been successfully used as a catalyst precursor for an intramolecular Heck-type reaction generating six-membered ring D analogues of the pentacyclic alkaloid cephalotaxine in high yields (Scheme 6).[37]

Benzothiazole palladacycles such as **16** have been used as catalysts in a three-component cascade process (Scheme 7) yielding 1-substituted styrenes in high yields (82−92%) under relatively mild reaction conditions (80 °C, 10 h).[27]

Optically active sulfur-containing palladacycle **10** promotes the arylation of 3,4-dihydro-2*H*-pyran under mild reaction conditions, albeit without any asymmetric induction (Scheme 8). This suggests that the palladacyclic moiety is probably not present in the catalytically active species.[38]

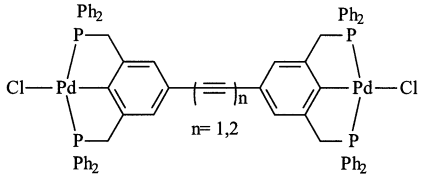
It is often assumed that the mechanism[39] of the Heck reaction involves the in situ generation of a Pd^0 species, which undergoes oxidative addition of the aryl halide yielding a Pd^{II}−aryl intermediate. Coordination of the olefin and its migratory insertion into the Pd−aryl bond leads to a Pd^{II}−alkyl complex. β-Hydrogen elimination affords the arylated olefin and a Pd−H species, which, through reductive elimination, regenerates the Pd^0 catalytically active species.[9]

The cyclopalladated moiety could sometimes be isolated unchanged after catalysis and in certain cases it was recycled.[22,28] It has also been observed that the Pd−C bond of these palladacycles is usually unreactive towards C=C units. Hence, no reduction of Pd^{II} to Pd^0 should occur through, for instance, a reductive elimination of HX following the β-elimination process of the cyclopalladated ligand coupled with the olefin. Moreover, since in most of these cases no formation of metallic palladium was noted, an alternative mechanism involving Pd^{II}/Pd^{IV} has recently been proposed by Shaw[19] and has been adapted for phosphorus-containing palladacycles such as **7**.[21] The key step in this mechanism is a reversible nucleophilic attack on the Pd^{II}−olefin complex by acetate or halide anions generating an electron-rich Pd^{II} species, which then undergoes oxidative addition of the aryl halide. Loss of the nucleophile fol-

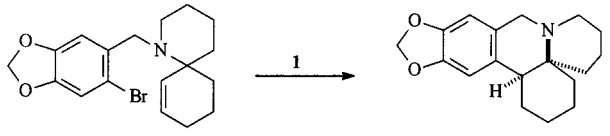
Table 1. Palladacycles which promote the Heck arylation reaction (Scheme 3)

Entry	Pd compd.	R	X	T [°C]	t [h]	Base	Conv. (%)	TON (10^3)	TOF [h^{-1}]	Ref.
1	**1**	CO_2Bu	Br	140	48	NaOAc	99	9.8	204	[12]
2	**2**	CO_2Bu	Br	140	18	NaOAc	51	0.25	14	[16]
3	**3**	CO_2Me	I	95	312	NBu_3	56	1120	3590	[13]
4	**3**	Ph	I	120	120	NBu_3	65	650	5417	[13]
5	**3**	Ph	Br	115	30	NBu_3	77	0.77	26	[13]
6	**4**	CO_2Me	I	140	350	Na_2CO_3	91	520	1487	[17]
7	**5**	CO_2Me	I	140	40	Na_2CO_3	95	529	13217	[17]
8	**5**	CO_2Me	Br	140	63	Na_2CO_3	93	133	2109	[17]
9	**6**	CO_2Bu	I	180	22	Na_2CO_3	89	8900	404500	[15]
10	**8**	CO_2Me	I	140	24	NEt_3	90	45	1875	[29]
11	**9**	CO_2Me	I	80	60	NEt_3	–	70	1167	[28]
12	**10**	CO_2Me	I	140	1	NEt_3	94	47	47000	[29]
13	**10**	CO_2Me	Br	170	8	NEt_3	75	37	46875	[29]
14	**11**	CO_2Me	I	140	18	NEt_3	100	1429	79389	[22]
15	**11**	CO_2Me	Br	140	130	Na_2CO_3	93	133	1022	[22]
16	**12**	CO_2Me	I	110	12	NEt_3	99	100	8333	[24]
17	**12**	Ph	Br	150	1	K_2CO_3	96	0.48	483	[25]
18	**13**	Ph	I	140	120	N^nPr_3	91	91	758	[26]
19	**14**	Ph	I	140	11	N^nPr_3	100	15.6	1420	[26]
20	**15**	CO_2Bu	I	110	48	K_2CO_3	100	2000	41667	[27]
21	**16**	CO_2Bu	I	90	48	K_2CO_3	90	100	2083	[27]
22	**17**	CO_2Et	Br	130	34	K_2CO_3	90	90	2647	[25]
23	**1**	CO_2Bu	[a]	140	48	NaOAc	93	0.087	1.8	[10]
24	**10**	CO_2Bu	[a]	170	6	NaOAc	61	30500	5082	[29]
25	**1**	CO_2Bu	[b]	130	24	NaOAc	90	80.1	34	[12]
26	**10**	CO_2Bu	[c]	170	2	NaOAc	49	490	245	[29]
27	**7**	Ph	[b]	180	24	CsOAc	81	122	5.1	[21]
28	**7**	Ph	Cl	180	24	CsOAc	99	149	6.2	[21]
29	**7**	Ph	[d]	180	24	CsOAc	86	129	5.4	[21]
30	**12**	Ph	[c]	150	42	K_2CO_3	71	70	1166	[25]

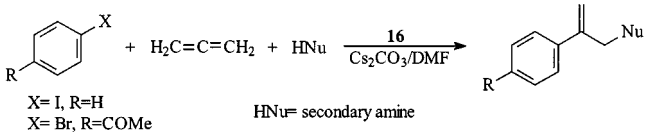
[a] 4-Bromoanisole. – [b] 4-Chlorobenzaldehyde. – [c] 4-Nitrochlorobenzene. – [d] 4-Chloroanisole.



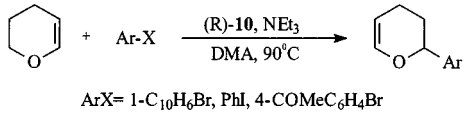
Scheme 5. A binuclear phosphapalladacycle



Scheme 6. Palladacycle **1** mediated intramolecular Heck reaction



Scheme 7. A three-component cascade process



Scheme 8. Arylation of 3,4-dihydro-2*H*-pyran

lowed by migratory insertion of the thus generated C=C bond into the Pd^{IV}–aryl bond, β-hydrogen elimination, and reductive elimination of HX then produces the arylated olefin and regenerates the Pd^{II} catalyst. However, one important feature disfavouring this suggestion is the lack of precedence for observing the oxidative addition of aryl halides to Pd^{II} as compared to the now well-known oxidative addition of alkyl halides to organopalladium(II) species.[40] Nevertheless, it would seem that a Pd^{IV} intermediate has recently been isolated in the arylation of norbornene (see later).[41] In the case of palladacycles of type **1**, Herrmann et al. have suggested that they constitute a reservoir of highly active Pd^0 species, which are generated by heterolytic cleavage of the Pd–C bond with subsequent reduction to Pd^0.[7] Very recently, in the case of cyclopalladated imine complexes such as **13** and **14** (Scheme 4), the involvement of Pd^0 nanoparticles originating from the immobilized palladacycles has been proposed.[26] It is unclear as to which mechanism is the most likely to be operative. Further studies to strengthen one or other of the proposals are still required.

Suzuki and Stille Cross-Coupling Reactions

The cross-coupling of aryl halides with organoboron compounds (Suzuki cross-coupling reaction)[42] or or-

ganotin compounds (Stille cross-coupling reaction)[43] is mediated by a variety of palladium catalyst precursors, the latter usually bearing phosphane ligands.

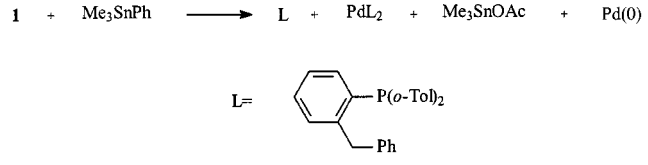
Suzuki and Stille cross-couplings have only been investigated with a few palladacycles (Table 2).

Table 2. Suzuki and Stille cross-couplings catalysed by palladacycles (ArX + PhM → ArPh + MX)

Entry	Pd compd. (%)	M	Ar	X	base	*T* [°C]	*t* [h]	Yield (%)	Ref.
1	**1** (10^{-3})	$B(OH)_2$	4-$MeCOC_6H_4$	Br	K_2CO_3	130	20	74	[20]
2	**1** (10^{-1})	$B(OH)_2$	Ph	Br	K_2CO_3	130	20	99	[20]
3	**1** (10^{-2})	$B(OH)_2$	4-$MeOC_6H_4$	Br	K_2CO_3	130	20	76	[20]
4	**1** (10^{-1})	$B(OH)_2$	4-$MeCOC_6H_4$	Cl	K_2CO_3	130	20	82	[20]
5	**12** (10^{-1})	$B(OH)_2$	4-$MeCOC_6H_4$	Br	K_2CO_3	110	0.5	97	[24]
6	**11** (10^{-6})	$B(OH)_2$	4-$MeCOC_6H_4$	Br	K_2CO_3	130	16	84	[23]
7	**11** (5×10^{-6})	$B(OH)_2$	Ph	Br	K_2CO_3	130	3	90	[23]
8	**11** (5×10^{-6})	$B(OH)_2$	4-$MeOC_6H_4$	Br	K_2CO_3	130	3	60	[23]
9	**10** (0.5)	$B(OH)_2$	4-$MeOC_6H_4$	Br	K_3PO_4	130	4	90	[30]
10	**10** (0.5)	$B(OH)_2$	4-$MeOC_6H_4$	Br	K_3PO_4	25	38	95	[30]
11	**6** (10^{-2})	$B(OH)_2$	4-$MeOC_6H_4$	Br	K_2CO_3	130	18	87	[44]
12	**10** (0.5)	$B(OH)_2$	4-NCC_6H_4	Cl	K_3PO_4	25	16	92	[30]
13	**10** (0.5)	$B(OH)_2$	Ph	Cl	K_3PO_4	130	22	46	[30]
14	**6** (10^{-2})	$B(OH)_2$	4-$NO_2C_6H_4$	Cl	K_2CO_3	130	18	43	[44]
15	**1** (2.0)	$SnMe_3$	Ph	Br	−	110	24	97	[7]
16	**1** (5.0)	$SnMe_3$	4-$MeCOC_6H_4$	Br	−	100	4	96	[45]
17	**12** (3.0)	$SnMe_3$	4-$MeCOC_6H_4$	Br	−	110	5	95	[24]

Phospha- and nitrogen-palladacycles effectively promote the Suzuki cross-coupling of aryl bromides, albeit only at elevated temperatures (100−130 °C). It is important to note that $Pd(OAc)_2$ has also been shown to catalyse the Suzuki cross-coupling reaction of aryl bromides with high turnovers, and consequently these substrates (in particular 4-bromoacetophenone) are not useful benchmarks for testing new catalysts in Suzuki couplings.[46] Palladacycle **12** was only tested in the coupling of 4-bromoacetophenone with phenylboronic acid at 110 °C.[24] However, sulfur-containing palladacycles catalyse these couplings at room temperature (see Table 2, Entries 10 and 12) and, moreover, they also promote the reaction of less reactive aryl chlorides, although higher reaction temperatures are required in the latter cases. This system represents the most effective phosphane-free catalyst system for the room temperature Suzuki cross-coupling reported to date.[47]

Mechanistic insights into the Stille coupling have been obtained by monitoring the reaction of palladacycle **1** with Me_3SnPh by NMR spectroscopy. The investigators observed the formation of free and palladium-ligated arylated phosphane and P(*o*Tol)$_3$ ligands (Scheme 9).[37]

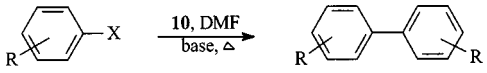


Scheme 9. The formation of Pd^0 catalytically active species

These observations suggested that the catalytically active species in the Stille and Suzuki couplings possess either P(*o*-Tol)$_3$ or modified PAr(*o*Tol)$_2$ ligands, or a combination of the two, associated with Pd^0. In these cases, the palladacycle may act as a reservoir of catalytically active Pd^0 species.

Phosphapalladacycle **1** has also been shown to catalyse the coupling of functionalized bromoarenes to a polystyrene-bound aryl tributylstannane. This reaction provides a convenient method for the synthesis of several biaryl compounds on resins.[48]

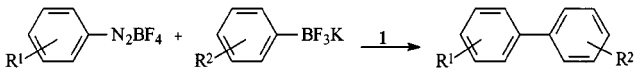
The phosphapalladacycle **1** is also an effective catalyst precursor for other coupling reactions, such as Grignard and Negishi-type protocols.[7] Very recently, it was reported that cyclopalladated oximes such as **12** also promote the Ullmann homo-coupling reaction of 4-iodo- and 4-bromoacetophenone with modest TONs (up to 50).[24] In contrast, sulfur-containing palladacycles such as **10** (Scheme 4) efficiently catalyse the homo-coupling of various aryl iodides and bromides in high yields (> 90%, Scheme 10).[49]



R= H, Me, COMe, OMe, NO_2, etc.; X= Br, I.

Scheme 10. Ullmann homo-coupling promoted by palladacycle **10**

Palladacycle **1** has been shown to be one of the most efficient of the classical Pd catalysts for a Suzuki-like reaction between Ar−N_2BF_4 and Ar′−BF_3K affording the expected biphenyl Ar−Ar′ as a result of a cross-coupling (Scheme 11).[50]

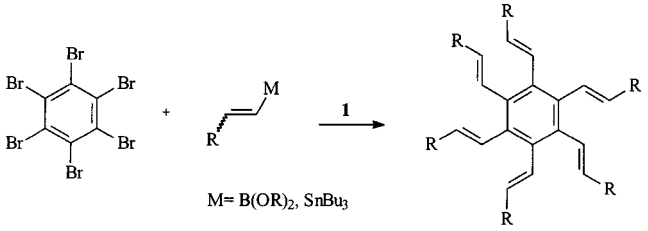


Scheme 11. Cross-coupling of organotrifluoroborates

The catalyst is usually active at low concentrations (0.1%) and the reactions proved successful with substrates bearing either electron-withdrawing or electron-donating substituents. The same catalyst was also effectively used in the formation of styrene and stilbene derivatives by the reac-

tions of $Ar-N_2BF_4$ with vinyl and styryl trifluoroborates, respectively.

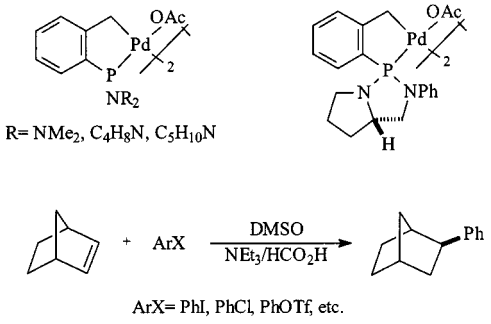
Palladacycle **1** was also used in the sixfold alkenylation of hexabromobenzene through Suzuki and Stille couplings (Scheme 12), generating hexakis(3,3-dimethyl-1-butenyl)-benzene in good yields.[51]



Scheme 12. Sixfold coupling of hexabromobenzene catalysed by palladacycle **1**

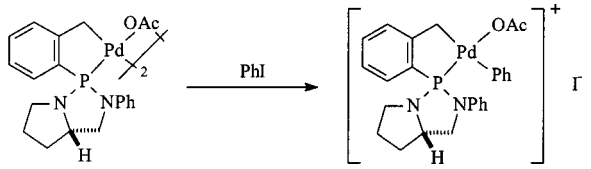
Hydroarylation of Olefins

Cyclopalladated aminophosphane-based ligand systems (Scheme 13) are highly efficient catalysts for the hydroarylation of norbornene, giving rise to exceptionally high TONs. Indeed, the latter can reach an incredible and unprecedented 10^{10}, corresponding to a catalyst loading of as little as 5×10^{-9} mol-%.[41,52]



Scheme 13. Hydroarylation of norbornene catalysed by a phosphapalladacycle

An enantioselective variant has been developed, giving modest *ee* values (up to 25%) in the hydroarylation of norbornene with phenyl triflate.[41] By treating the phosphapalladacycle with iodobenzene, the authors isolated a rather strange organopalladium species (Scheme 14).

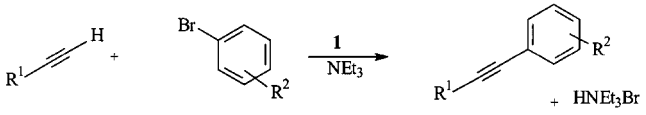


Scheme 14. The formation of a Pd^{IV} intermediate

Its crystal structure suggested the presence of a cationic tetracoordinate Pd^{IV} species having an iodide as a counterion. Although no details have been given concerning the behaviour of this product, confirmation of this preliminary result would provide a strong argument for the existence of a $Pd^{II}-Pd^{IV}$ pathway in, for example, the Heck reaction.

Sonogashira Reaction

The palladium-catalysed coupling of aryl iodides and bromides with terminal alkynes is a well-established method for the preparation of disubstituted alkynes (Scheme 15).[53] A wide variety of palladium catalyst precursors efficiently promote this reaction, usually in the presence of CuI as a co-catalyst. Not surprisingly, phosphorus-,[54] nitrogen-,[23] and sulfur-containing [55] palladacycles mediate this coupling reaction. However, in the case of palladacycle **1**, the reaction is catalysed in the absence of a co-catalyst and using a very low catalyst loading. Turnover numbers up to 8000 have been reported in the coupling of 4-bromoacetophenone with phenylacetylene.[54]

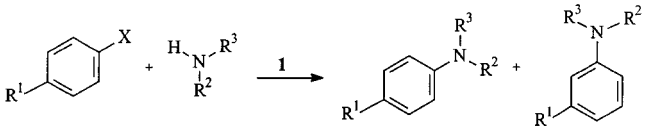


Scheme 15. The Sonogashira coupling reaction

Here also, a mechanism involving Pd^{IV} species has been postulated as being operative in the case of palladacycle **1**.

Amination of Aryl Halides[56,57]

Phosphapalladacycles were among the first palladium catalyst precursors to be used to promote the amination of aryl halides leading to substituted anilines (Scheme 16).[37,58] The reactions of secondary amines with bromoarenes and activated chloroarenes are efficiently catalysed by palladacycle **1** using NaO*t*Bu or KO*t*Bu as a base at temperatures in the range 100−130 °C.[58]

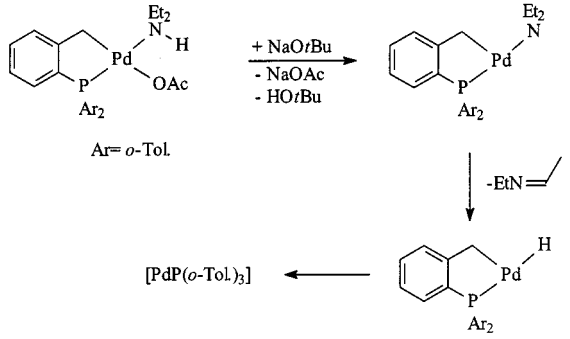


X= Br, R^1= COMe, CN, F, Me, H, OMe; amine= piperidine, $HNBu_2$, $HNPh_2$, $HNiPr_2$

X= Cl, R^1= CF_3, COPh; amine= piperidine, $HNBu_2$, $HNPh_2$, $HNiPr_2$, etc.

Scheme 16. Amination of aryl halides promoted by palladacycle **1**

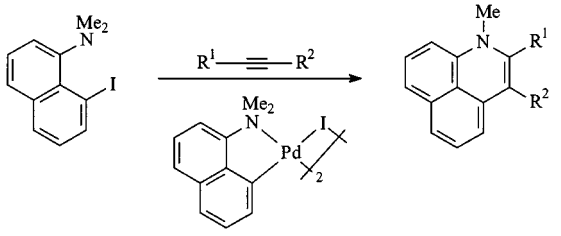
It is interesting to note that the *meta* isomer was also obtained, and that a side mechanism involving aryne intermediates was shown to be operative by running the reaction in the absence of a catalyst. Elegant studies showed that in these cases the palladacycle **1** again serves as a reservoir of catalytically active Pd^0−phosphane species. The latter are probably formed through a β-hydrogen elimination followed by a reductive elimination process from a palladium amide complex (Scheme 17).



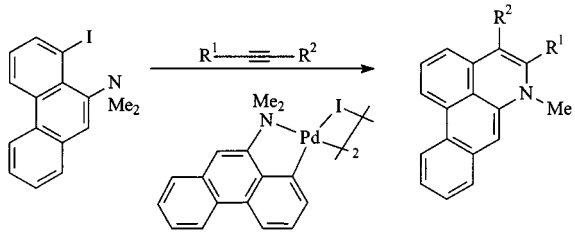
Scheme 17. Postulated mechanism for the generation of Pd^0 species from palladacycle **1** in the presence of $HNEt_2$

Hetero- and Carbo-Annulation Reactions

Palladacycles are also effective catalyst precursors for the preparation of *N*-methylbenzo[*d*,*e*]quinolines,[59] *N*-methyldibenzo[*d*,*e*,*g*]quinolines,[60] and 2,3-diphenylindenone.[7] Cyclopalladated (dimethylamino)naphthalene (Scheme 18) and -phenanthrene complexes (Scheme 19) were shown to mediate the reaction of internal alkynes with (dimethylamino)iodonaphthalene and -phenanthrene derivatives, respectively, leading to quinolines in reasonable to good yields (Schemes 18 and 19).

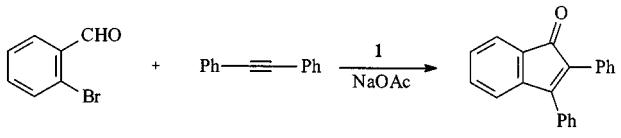


Scheme 18. Nitrogen palladacycle catalysed quinoline synthesis



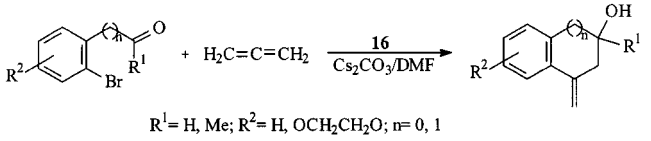
Scheme 19. Pd-catalysed construction of the B-fragment of the Aporphine skeleton

It has recently been shown that 2,3-diphenylindenone can be prepared by the reaction of 2-bromobenzaldehyde with diphenylacetylene in the presence of 0.1 mol-% of palladacycle **1** (Scheme 20).[7]



Scheme 20. Synthesis of a substituted indenone catalysed by **1**

Palladacycles of type **16** (Scheme 4) have been used to generate catalytically active Pd^0 species for the intramolecular nucleophilic addition of allylic intermediates, generated from allene, to 2-bromoaryl aldehydes or ketones (Scheme 21).[61]

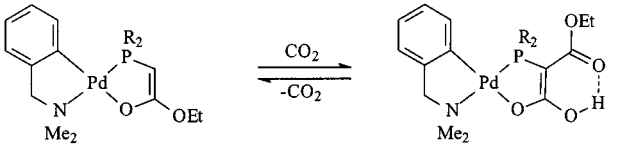


Scheme 21. Carbopalladation of allenes

Despite the high potential of this method for the synthesis of carbo- and heterocycles, which starts from easily accessible substrates, few examples of these types of reactions have appeared. Nevertheless, many related processes are mediated by catalytic systems based on palladium acetate.[62]

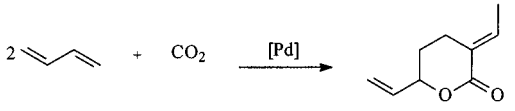
Telomerization of Dienes

Cyclopalladated phosphane enolates bearing *N*,*N*-dimethylbenzylamine ligands (Scheme 22) have been shown to be reversible CO_2 carriers at room temperature.[63]



Scheme 22. Phosphane enolate palladacycles as reversible CO_2 carriers (R = Ph, Cy)

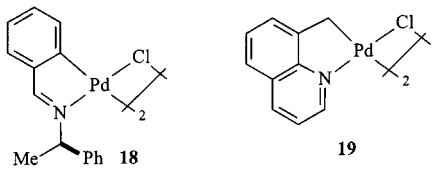
These complexes catalyse the telomerization of butadiene with CO_2 under relatively mild reaction conditions (20 bar CO_2, 90 °C) to furnish the lactone 2-ethylidene-6-hepten-5-olide with good selectivity (up to 93%) (Scheme 23).[64]



Scheme 23. Telomerization of butadiene with CO_2

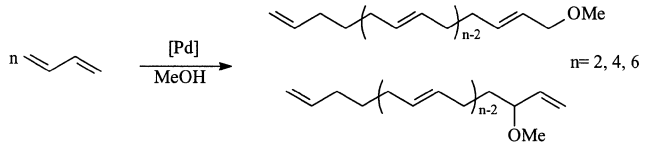
These complexes were the first examples of CO_2 carriers showing catalytic activity towards CO_2. It is also interesting to note that the cyclopalladated unit was isolated intact after catalysis, demonstrating its ancillary behaviour.

Not surprisingly, nitrogen-containing palladacycles, such as those derived from amines, imines, and quinolines (Scheme 24), promote the selective telomerization of 1,3-dienes with alcohols.[65,66]



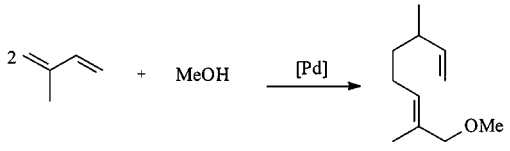
Scheme 24. Palladacycle catalyst precursors for the telomerization of 1,3-dienes

The cationic palladacycles derived from **17**−**19** mediate the telomerization of butadiene with methanol giving telomers containing 2−6 diene units (Scheme 25).



Scheme 25. Palladacycle-catalysed telomerization of butadiene with methanol

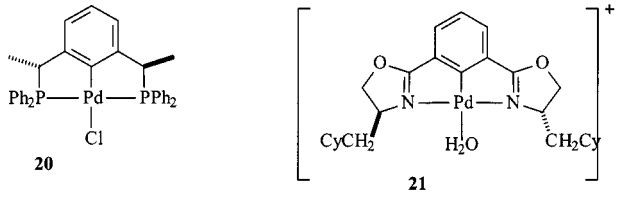
The selectivity was found to be strongly influenced by the nature of the palladacycle catalyst precursor, suggesting that the ligands it bears are present in the catalytically active species. Selectivities of up to 61% in high telomers (4 and 6 monomeric units) could be achieved using palladacycle **17**.[66] This selectivity is superior to that obtained with other palladium catalysts such as π-allyl complexes.[67] Palladacycle **16** was also shown to be effective in the generation of catalytic species for the telomerization of isoprene with methanol, yielding 1-methoxy-2,6-dimethyl-2,7-octadiene with selectivities of up to 67% (Scheme 26).[65]



Scheme 26. Telomerization of isoprene with methanol

Aldol-Type Reactions[68−70]

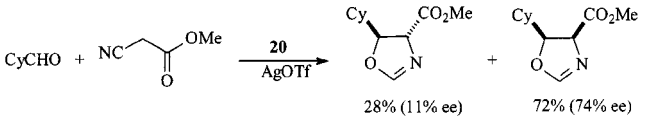
Cyclopalladated complexes containing PCP and NCN ligands have recently been utilized in asymmetric aldol-type reactions (Scheme 27).



Scheme 27. Palladacycles used as catalyst precursors for aldol-type reactions

The rationale behind the deployment of such complexes stemmed from the observation that classical ligands, including BINAP and DIOP, led to poor selectivities in these reactions, which was attributed to the fact that the key enantioselective step occurred too far away from the chiral pocket. PCP and NCN ligand-based systems offer a deeper chiral pocket, leading to some enantio-discrimination without the need for pendant groups designed for secondary interactions.[71]

To carry out the aforementioned reaction using methyl isocyanoacetate and various aldehydes (Scheme 28), it was found that the cyclopalladated complex had to be activated by halide abstraction with a silver salt.



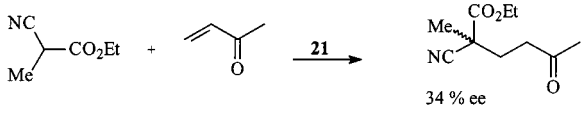
Scheme 28. Asymmetric aldol reaction catalysed by a cyclopalladated PCP complex

Some pertinent observations were made regarding this system:

(i) Palladium complexes are more effective than their platinum congeners. Moreover, *cis* selectivity is higher than that with similar related platinum complexes.[72]

(ii) THF is the solvent of choice; other variations, such as the order of addition of the reactants or the nature of the base used, have little effect on the reaction outcome.

Cyclopalladated NCN ligands were found to be ineffective in the above reaction and also in Diels−Alder reactions. However, they were found to be effective in the formation of a quaternary centre through chiral Michael addition (Scheme 29).

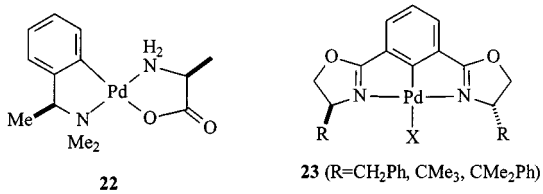


Scheme 29. Asymmetric Michael addition mediated by an NCN palladacycle

For these reactions, selectivities were found to be higher in toluene and increased when bulky substituents were present on the oxazoline ligands, although reaction times were often longer. The reaction is presumed to proceed through a Pd^{II} intermediate acting as a Lewis acid. An immobilized catalyst system is envisaged as offering an improvement in the near future.

Cyclopropanation

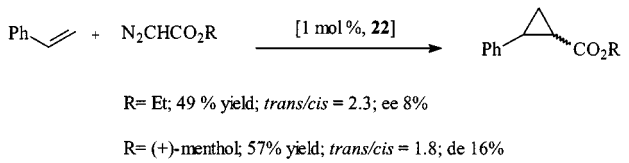
Recent reports have shown that neutral acetylacetonato and amino acid chelated cyclopalladated complexes (Scheme 30) are capable of catalysing cyclopropanation reactions.[73]



Scheme 30. Chiral palladacyclic catalyst precursors used in cyclopropanation reactions

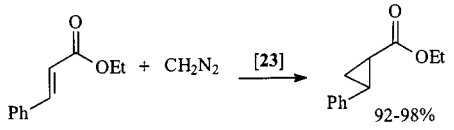
The enantioselectivities achieved with these palladacycles are poor, with the highest *ee* values being less than 10%. Diastereoselectivities reached 20% when a menthol-con-

taining diazoacetate derivative was used as a chiral starting material (Scheme 31).



Scheme 31. Cyclopropanation catalysed by a nonracemic benzylamine amino acid palladacycle

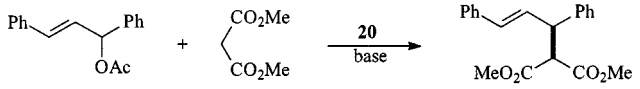
Non-racemic aryloxazoline palladacycles such as **21** have been shown to efficiently promote the diazomethane-based cylopropanation reaction (Scheme 32), but all the obtained products were racemic.[74]



Scheme 32. Cyclopropanation catalysed by aryloxazoline palladacycles

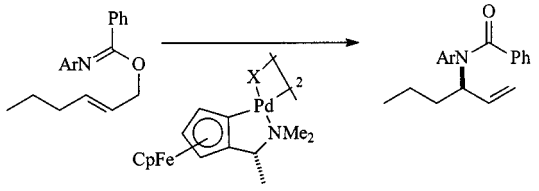
Allylic Substitution and Rearrangement[75]

Archetypal allylic substitutions of 1,3-diphenylprop-2-enyl acetate were investigated with PCP ligands such as that used in palladacycle **18** and modest enantioselectivities were achieved (Scheme 33).[76] Here though, when associated with π-allylpalladium complexes, the ligands are likely to adopt a bidentate PP-type coordination mode, taking them beyond the scope of this review.



Scheme 33. Allylic substitution reaction

Functionalized allylic alcohols can be converted into chiral allylic amine derivatives by a palladium-catalysed 3,3-sigmatropic rearrangement.[77] The achiral version of this reaction is effected by $PdCl_2(PhCN)_2$ and the authors chose palladium complexes containing an anionic ligand as a "chiral mimic" of the aforementioned complex.[78] Planar chiral ferrocene derivatives (Scheme 34) proved to be the most effective catalysts, affording excellent enantioselectivities with good reaction rates and yields, whilst avoiding side products due to 1,3-rearrangements (e.g. hexadienes).



Scheme 34. Chiral planar ferrocenyl palladacycle mediated allylic rearrangements

Conclusions and Perspectives

It is quite fitting that the majority of the work cited herein has been published during the last five years as our goal has been to demonstrate that the chemistry of cyclopalladated complexes, which is still in its infancy in terms of catalytic applications, will undoubtedly have a lot more to offer in the near future.

It is clear from the state of the art that further detailed mechanistic studies will have to be performed in order to unambiguously determine whether or not the cyclopalladated ligand is indeed attached to the catalytically active Pd species or whether these compounds are merely powerful sources of ligand-stabilized Pd^0 in which the Pd−C bond has been cleaved. This will aid the rational design of ligands and complexes, thereby leading to even more efficient palladium-containing catalysts. With TONs reaching 10^5 and even 10^{10} in some cases, more applied synthetic (e.g. natural products) and industrial applications can soon be anticipated. Palladacycles such as **1** are now commercially available and general procedures for their preparation are part of classical organometallic procedures.[79]

Acknowledgments

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