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Invited review

Transition metal-catalysed organic reactions promoted by chelating or metallacycle-forming substrates

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Abstract

Chelating or metallacycle-forming substrates are very useful for directing organometallic reactions. This review covers the more recent research that has been carried out in the authors' laboratory. Rhodium(I)- and (III)-catalysed reactions of C–C coupling of butadiene with *N*-allylamides or *N*-alkylbutenamides are described. These reactions are controlled by the size and strength of the chelate ring formed by double-bond insertion into the crotyl–rhodium bond (formed from butadiene) and their regioselectivity can change with the oxidation state of the metal. Rhodium(I)-catalysed reactions of butadiene with enamides are also chelation controlled and lead to different products, depending on the substituents at nitrogen. Cobalt(II) metallacycles have been utilized for promoting some organic reactions. It has been shown that alkenes can be catalytically incorporated into cobaltacyclopentadiene rings, that spirocycles can be obtained from diynes, carbon monoxide and acrylic esters and that a Pauson–Khand-type reaction can be combined with a Michael-type reaction to prepare catalytically new cyclopentenones. The use of palladacycles, derived from norbornene insertion into aryl–palladium bonds, followed by cyclization, has allowed the selective functionalization of either end of the metallacycle and the formation of condensed rings. Conversion of a palladium(II) into a palladium(IV) metallacycle, and catalytic processes involving these intermediates, have been achieved. The formation of alkylaromatic palladacycles has also been exploited for the selective *meta* functionalization of the aromatic moiety by means of alkyl groups, accompanied by expulsion of the norbornene molecule.

Keywords: Rhodium; Palladium; Cobalt; Metallacycles; Catalysis

1. Introduction

The aim of this paper is to review some general criteria we have been using in our research to promote metal-catalysed multistep organic reactions. As far back as 1957 [1], the nickel-catalysed stereoselective addition of allyl compounds and carbon monoxide to acetylene was reported. It involved two C–C bond-forming steps with the former determining the conditions for the occurrence of the latter. The synthesis of methyl (*Z*)-hexa-2,5-dienoate is an example:

$$CH_2{=}CHCH_2Cl + HC{\equiv}CH + CO + MeOH \xrightarrow{Ni^0} (Z)CH_2{=}CHCH_2CH{=}CHCO_2Me + HCl \quad (1)$$

Multistep reactions of this type were extended to a variety of halides or esters and of alkynes and alkenes, with or without carbon monoxide [2], and to other metals and ligands [3], and were later called sequential, cascade, tandem, domino or zipper reactions [4].

From the beginning we were concerned to find tools to promote these reactions in view of the high selectivity and observed that, much as in nature, the substrate itself could provide an efficient way to direct catalytic processes chemo-, regio- and stereoselectively [5].

We shall concentrate on the following topics from our recent work: (1) rhodium-catalysed C–C bond formation driven by chelating substrates and (2) cobalt- or palladium-catalysed C–C bond formation driven by metallacycles.

2. Rhodium-catalysed C–C bond formation driven by chelating substrates

Some insertion reactions do not proceed at all under certain conditions, but do occur if a chelating intermedi-

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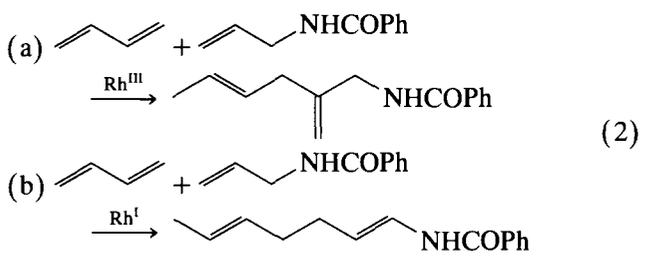
ate is formed. Typical examples in nickel [2,6] and rhodium [7] chemistry were described by us several years ago. Our recent work [8] was concentrated on the use of chelating substrates containing amide groups. These functions had been used in previous work as directing groups for selective hydrogenation [9], carbonylation [10] and alkylation [11] processes. We showed [8] that chelating substrates such as *N*-allylamides and 3-butenamides undergo rhodium-catalysed insertion reactions of the double bond to give a metal-bonded allyl group. Surprisingly, *N*-allylamides of organic acids displayed opposite regioselectvity, depending on whether the rhodium catalyst was present as rhodium trichloride alone or in association with sodium hydrogencarbonate. The latter condition favoured reduction to rhodium(I) (Eq. (2)), as we shall see later. In the former case butadiene attacked the internal carbon atom of the double bond exclusively, while in the latter only the terminal carbon was affected. In the examples reported below, the yield of reaction (2a) ($RhCl_3$, ethanol, 95°C, 36 h, branched product) was 78% at 87% conversion and the isomerization of the starting allylamide to 1-propenylamide accounted for 9%, whereas for reaction 2b ($RhCl_3 + Na_2CO_3$, ethanol. 95°C, 24 h. linear product) the yield at 60% conversion was 50% of the 1*E*,5*E* and 7% of the 2*E*,5*E* isomers.



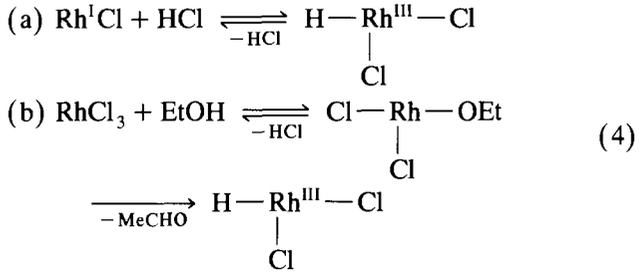
(2)

The reaction with rhodium(III) is a well known process, which has become commercial in the case of ethylene [12]. This reaction does not occur with rhodium(I) catalysts. Higher alkenes give a mixture of regioisomers [12]:

$$\text{(a)}\ CH_2{=}CHCH{=}CH_2 + CH_2{=}CH_2 \xrightarrow{Rh^{III}} CH_3CH{=}CHCH_2CH{=}CH_2$$

$$\text{(b)}\ CH_2{=}CHCH{=}CH_2 + CH_2{=}CHR \xrightarrow{Rh^{III}} CH_3CH{=}CHCH_2C(=CH_2)R + CH_3CH{=}CHCH_2CH{=}CHR \quad (3)$$

Cramer proposed a mechanism involving a rhodium(III) hydride, which triggers the reaction by hydride transfer to butadiene. Formation of the hydride can occur in two ways, starting from rhodium(I) or from rhodium(III):

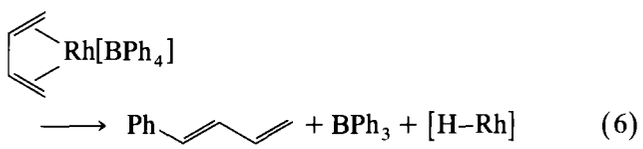


(4)

In contrast, we proposed [8] a rhodium(I) hydride [13] as the real catalyst of our reaction, on the basis of the complete regioselectivity towards the linear product. This reaction, which does not occur with non-chelating alkenes if the catalyst is a rhodium(I) complex, does indeed occur if allylamides of organic acids are used. The rhodium(I) hydride should form according to Eq. (5).

$$Rh^ICl + EtOH \underset{-HCl}{\rightleftharpoons} RhOEt \xrightarrow[-MeCHO]{} [Rh^IH] \quad (5)$$

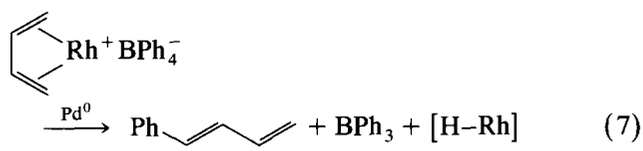
This pathway was substantiated by using $[HRh(PPh_3)_4]$ as catalyst. A limited but significant amount of linear product was obtained in spite of the negative effect of phosphines. However, the formation of a rhodium(I) hydride from rhodium trichloride is slow. We found a more efficient way to generate rhodium(I) hydride, based on the use of $[Rh(C_4H_6)]BPh_4$ (Eq. (6)).



(6)

In this case the yield of linear products (two stereoisomers) obtained according to Eq. (2) (together with a 2*E*,5*E* isomer) was 87% at 96% conversion at 95°C for 24 h in ethanol.

The latter pathway can be strongly accelerated by adding catalytic amounts of palladium(0). In spite of the negative effect of the phosphine ligands on the reaction, even $[Pd(PPh_3)_4]$ can be used advantageously. Addition of 10 mol% of Pd with respect to Rh led to a 96% conversion in 6 h, with the same product distribution. We thus obtain the following combination of reactions (Eqs. (7) and (8), ligands other than H and crotyl are omitted and only the *E* product is shown) [8]. Palladium cleaves a phenyl group from tetraphenylborate and couples it with butadiene [14]. The resulting rhodium-bonded phenylbutenyl group loses hydrogen to form the hydride, which in turn inserts butadiene and forms a crotyl group able to attack the chelated allylamide. The final liberation of the product regenerates the hydride for a new catalytic cycle.



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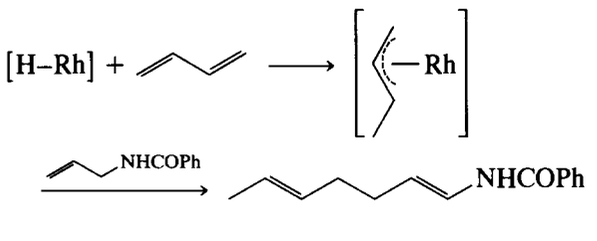
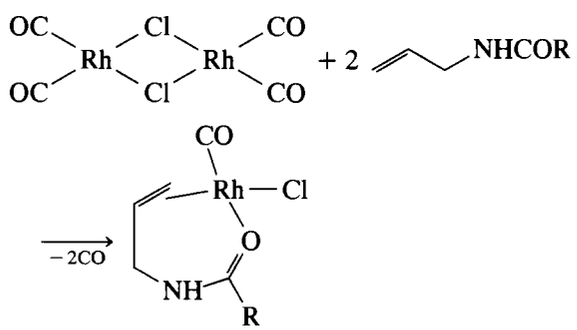


(8)

We named this combination "catalysis of catalysis" because the palladium-catalysed process leads to the rhodium catalyst active for the butadiene–allylamide reaction. The generality of the phenomenon of catalysis of catalysis deserves further investigation. In the literature there are hardly any examples of processes of this type. A related case may be the recent observation [15] that $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ oxidize pyridine to the *N*-oxide catalytically, thus generating a ligand which forms a new oxidation catalyst by coordination.

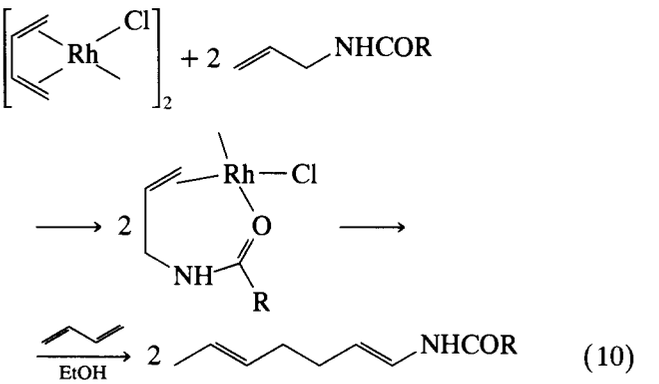
Returning to promotion by chelation, chelation played a fundamental role insofar as it allowed an otherwise impossible reaction with rhodium(I), and it rendered both the reaction with rhodium(I) and that with rhodium(III) regioselective, but in opposite senses. To clarify the promotion mechanism we prepared rhodium(I) complexes with *N*-allylamides and ascertained that the amide group was coordinated through oxygen (Eq. (9)).



(9)

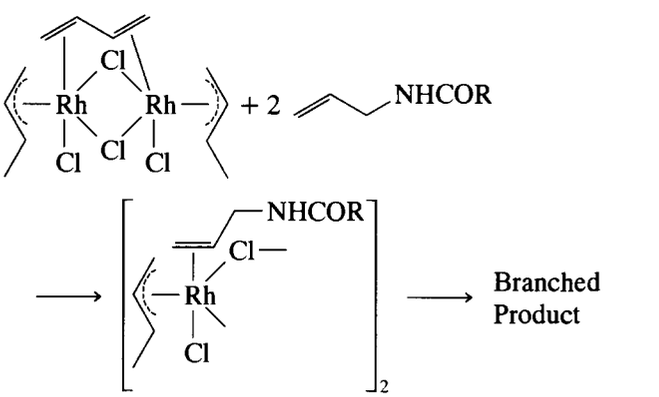
The structure of one of these complexes (*N*-allyl-*N*-methylbenzamide) has been determined [8]. It has a square-planar arrangement with the amide oxygen *trans* to the carbonyl and the chloride group *trans* to the double bond, which is perpendicular to the plane.

However, these complexes do not catalyse the reaction with butadiene because of the carbonyl group, which deactivates the catalyst. When we prepared complexes not containing the carbonyl group, such as the corresponding rhodium dimers, the reaction proceeded as expected, giving exclusively the linear product (Eq. (10)).

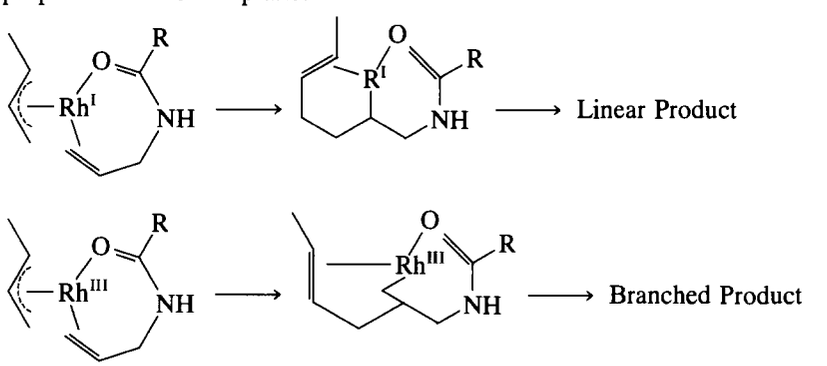


(10)

The preparation of amide complexes of rhodium(III) containing the crotyl group was attempted, starting from the complexes of Eq. 9 and crotyl chloride, but it failed because of coupling of the crotyl group. However, the resulting rhodium trichloride complex containing the carbonyl group and the amide still coordinated the amide through oxygen. We could obtain the desired reaction starting from a dimer described previously [16] (Eq. (11)).



(11)



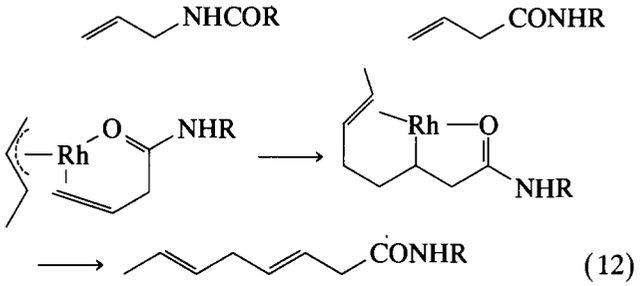
Scheme 1. Alternative pathways in chelation-controlled reactions of butadiene with *N*-allylamides.

We assume that the amide that was not coordinated through chelation in the original rhodium(III) dimer had to break the bridge to coordinate through oxygen. The result was the formation of the branched amide alone, together with crotyl group coupling products and isomerization products of the amide, presumably forming before breakage of the chloride bridge.

Based on these experiments, our interpretation of the formation of linear and branched products is as shown in Scheme 1, rhodium(I) hydride being assumed to be the real catalyst.

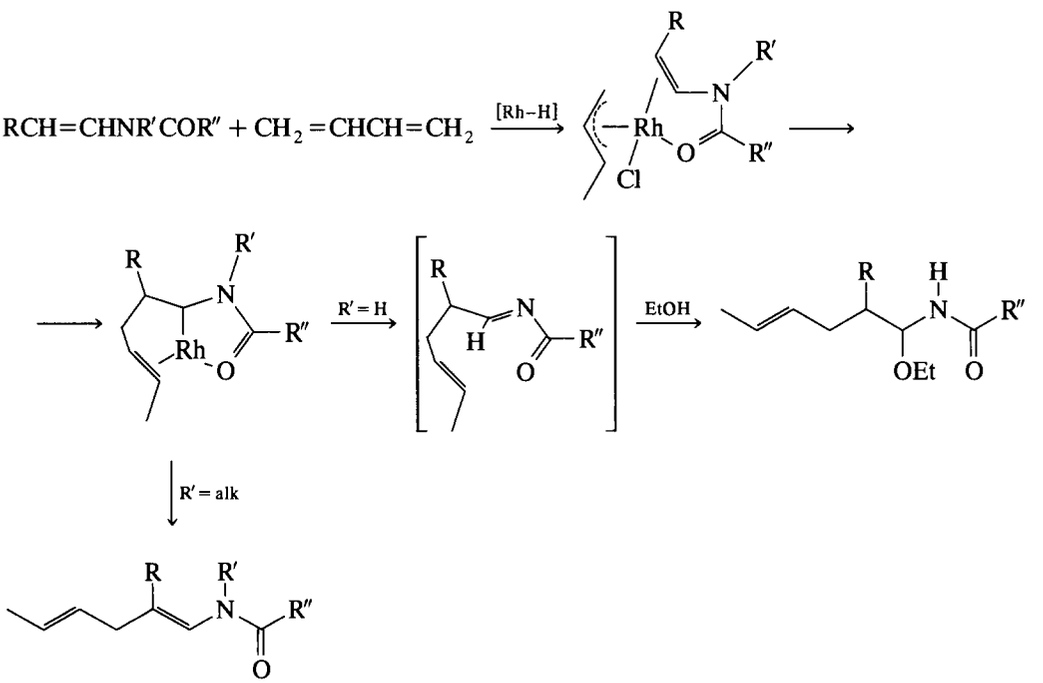
Chelation has opposite effects on rhodium(I) and rhodium(III). With the former the six-membered chelated ring formed by double bond insertion strongly favours the linear product. With the latter, which is able to cause double bond insertion even with non chelating substrates, as mentioned before, the seven-membered chelate merely reinforces the tendency of rhodium(III) to form a sigma bond with the primary rather than the secondary carbon atom of the inserting substrate. This is probably due to steric requirements and cannot be easily reversed except by the formation of a stronger chelate. In fact, if the NH–CO sequence of *N*-allylamides is reversed as in the amides of 3-butenoic acid, both rhodium(I) and rhodium(III) give the same linear product (Eq. (12)) because of the formation of a stronger five-membered chelate. Thus at 86% conversion and under the same conditions as adopted for *N*-allylamides, *N*-propylbutenamide gave with $RhCl_3$ a 74% yield of the linear product exclusively (2*E*, 6*E*:3*E*, 6*E* = 3:1).

N-allylamides of organic acids N-Alkylbutenamides



(12)

Recent extension of our studies to vinylamides produced new synthetic and mechanistic developments [17]. It was ascertained that butadiene attack (as a crotyl group) on the vinyl group proceeded analogously to what was observed with *N*-allylamides (Eq. (13)) only when nitrogen was trisubstituted (tertiary amides). If a proton was present at nitrogen the reaction proceeded in a completely different way, leading to *O*,*N*-acetals of unsaturated aldehydes by regioselective addition of a molecule of the alcohol used as solvent, to give a different insertion product (Eqs. (13) and (14)). For example, *N*-vinylacetamide reacted with butadiene at 70°C for 48 h in the presence of $[\{RhCl(C_2H_4)_2\}_2] + 2$ mol of $Na[BPh_4]$ to give 98% of the acetal of Eq. (13) (R = H, alkyl; R′ = H; R″ = alkyl or aryl), whereas *N*-methyl-*N*-vinylacetamide under the same reaction conditions except for the temperature (80°C) gave 73% of the first compound of Eq. (14) (two stereoisomers), 7% of a conjugated isomer and 9% of the second compound of Eq. (14) (resulting from double addition



Scheme 2. Alternative pathways in the chelation-controlled reaction of butadiene with enamides.

of butadiene, R = H, alkyl; R = alkyl; R = alkyl or aryl).

$$RCH{=}CHNR'COR'' + CH_2{=}CHCH{=}CH_2 + EtOH \xrightarrow{Rh^I} CH_3CH{=}CHCH_2CHRCH(OEt)NR'COR'' \quad (13)$$

$$RCH{=}CHNR'COR'' + CH_2{=}CHCH{=}CH_2 \xrightarrow{Rh^I} CH_3CH{=}CHCH_2CR{=}CHNR'COR'' + (CH_3CH{=}CHCH_2)_2C{=}CHNR'COR'' \quad (14)$$

The result is explained clearly by Scheme 2. The course of the reaction changes depending on the presence or absence of a substituent at nitrogen in the final step (β-hydrogen elimination). Two positions are involved, at C or at N, and the latter is strongly preferred. Alcohol addition to the N=C bond thus formed gives the acetal.

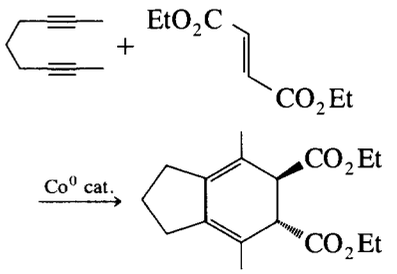
As shown by the X-ray structure of a rhodium(I)–enamide complex [18], the amido group chelates through oxygen. Chelation plays a determining role in the reaction of dienes with enamides, rhodium(I) not being effective with simple non-chelating alkenes.

3. Cobalt- or palladium-catalysed C–C bond formation driven by metallacycles

We have seen that chelation by the substrate has a powerful influence on the catalysis of regioselective reactions. The use of metallacycle-forming substrates also favours the catalysis and selectivity of organic reactions. Our work in this area goes back several years, but only recent developments in cobalt and palladium chemistry will be reported here.

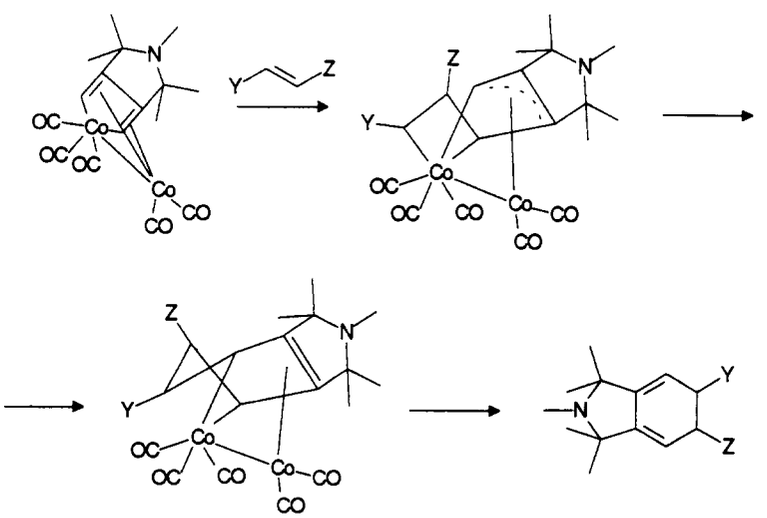
3.1. Intermediacy of cobaltacycle-forming substrates in the catalytic synthesis of cyclic organic molecules

Metallacycles obtained from alkynes and cobalt(I) complexes are well known, as is their intermediacy in catalytic reactions [19], such as the synthesis of aromatic compounds and pyridines. Reactions of alkynes with alkenes involving cobaltacyclopentadienes were shown by us to occur catalytically if cobalt(0) complexes were used [20]. Eq. (15) shows an example. In contrast, cobalt(I) gives stable cobalt(III) complexes. Cobalt(0) offers a better accessibility to the metal and a ready release of the products, thanks to weaker coordination to the cobalt(II) compound formed.

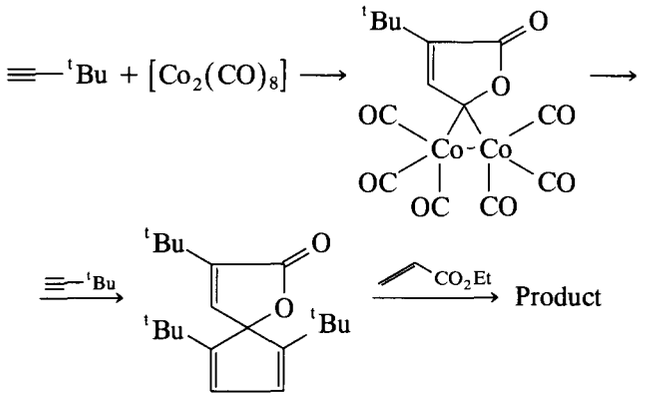


(15)

Since we isolated dimeric cobalt carbonyl complexes containing metallacycles formed from 1,6-diynes, which were able to incorporate activated alkenes according to Eq. (15), we proposed that the latter first added across a metal-to-cobalt bond, thus forming an allylic species stabilized by the other cobalt atom of the dimer. In a subsequent step, this intermediate should rearrange to a bicyclic ring, the release of which would liberate the organic product and the dimeric cobalt carbonyl. Scheme



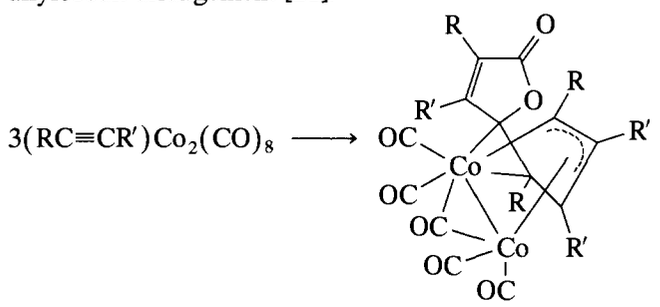
Scheme 3. Proposed pathway for the formation of condensed cyclohexadienes (exemplified for tetrahydroisoindole), via metallacycles of dimeric cobalt carbonyls.



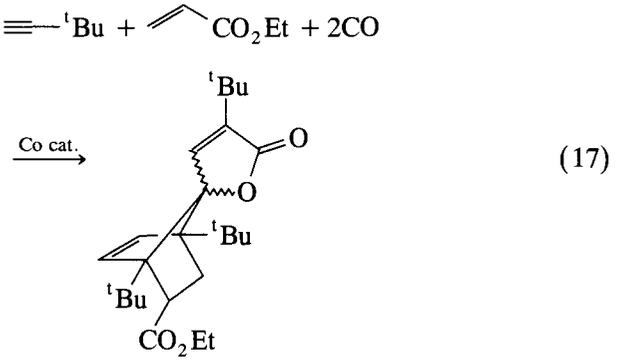
Scheme 4. Proposed pathway for the formation of the spirocycle of Eq. (17).

3 shows an example taken from the reaction of a 1,6-diyne, containing nitrogen in the chain.

Further support to our interpretation is the isolation of a dimeric species (Eq. (16)) containing a similar allylcobalt arrangement [21].

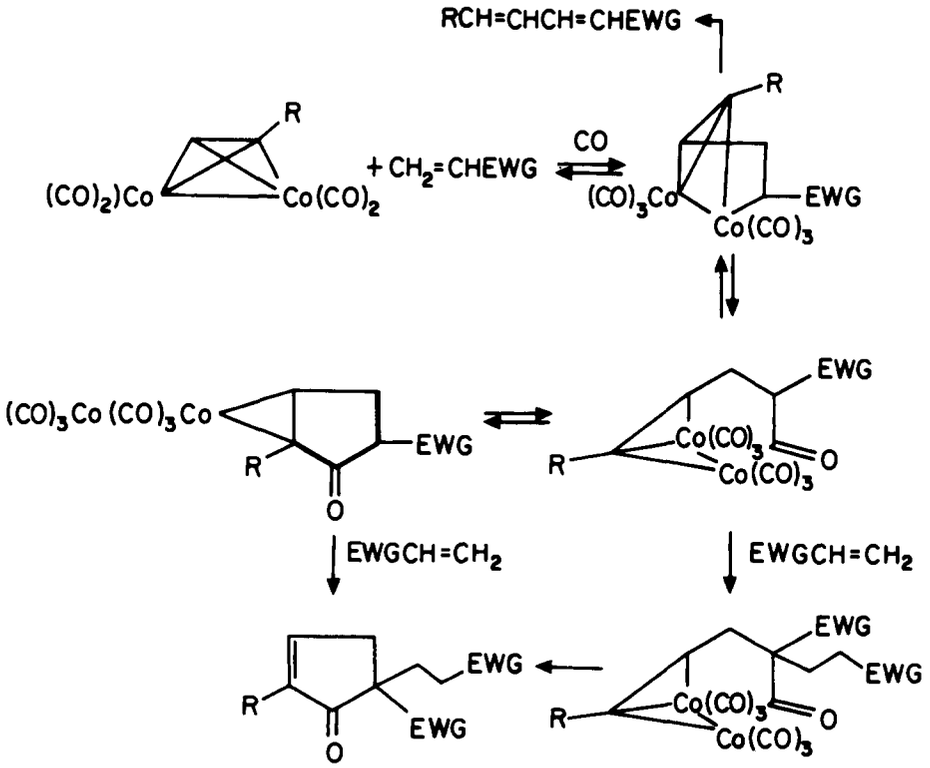


A more complex reaction occurs when dicobalt octacarbonyl is caused to react with *tert*-butylacetylene, carbon monoxide and ethyl acrylate [22]. In spite of the many steps involved, leading to the formation of eight new bonds, a spirotricyclic organic product is obtained in the remarkable yield of 65% (Eq. (17)).



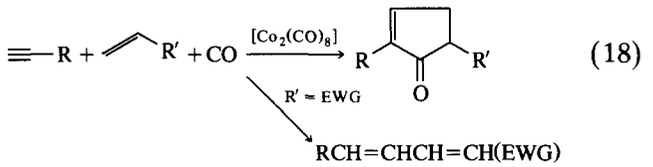
The course in Scheme 4 was proposed to account for the transformation observed. A known [23] lactonylidene complex should be initially formed, followed by addition of two molecules of the alkyne, elimination of a spiro compound and Diels–Alder reaction of the latter with the acrylic ester (Scheme 4).

So far we have seen reactions that are promoted by cobaltacycles formed from alkynes. Cobaltacyclopentenes formed from one alkyne and one alkene molecule are intermediates in the well known Pauson–Khand reaction [24]. It is also known that the reaction does not work with alkenes containing electron-



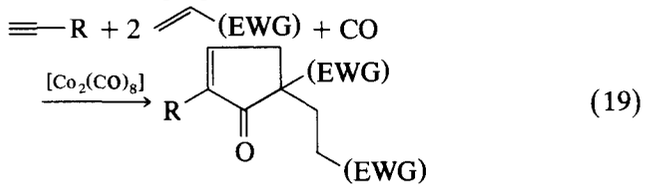
Scheme 5. Proposed pathway for the combination of Pauson–Khand and Michael reactions.

withdrawing groups (EWG) at the double bond (Eq. (18)).



(18)

It has now been found that (EWG)CH=CH_2 alkenes (EWG = alkylcarboxylate or CN) can be caused to react through formation of cobaltacyclopentenes if the intermediate cobaltacycle formed reversibly is trapped by another (EWG)CH=CH_2 molecule by a Michael-type reaction (Eq. (19)) [25]. Thus 1-hexyne reacted with methyl acrylate (as solvent) and carbon monoxide at 120°C and 40 bar in the presence of [$Co_2(CO)_8$] and of a base such as di-*tert*-butylpyridine to give 53% (isolated yield) of the product of Eq. (19). Scheme 5 describes the proposed mechanism.



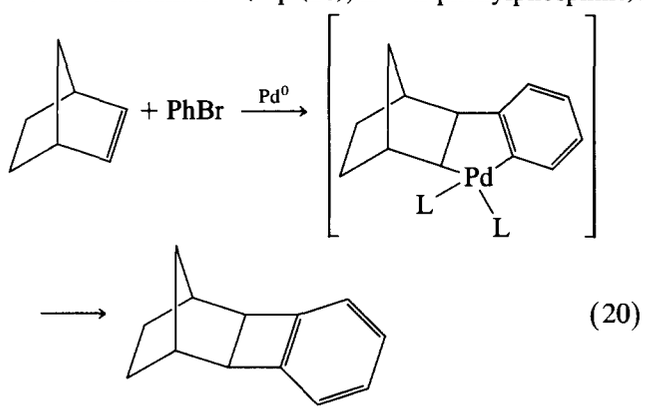
(19)

Assuming that the initial steps are similar to those generally accepted for the Pauson–Khand reaction [24], we postulate trapping of an intermediate by a second molecule of activated alkene, probably at the stage of the cobalt complex preceding the disfavoured cyclopentenone formation.

3.2. *Palladacycles as intermediates in site-selective functionalization of organic compounds*

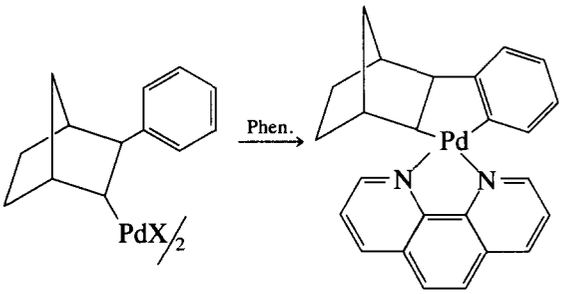
The chemistry of metallacycles has attracted much interest [26]. Our studies on palladacycles as intermediates in organic synthesis have led us to preparative methods and also to the isolation and characterization of the palladium complexes involved.

We reported for the first time palladium-catalysed ring-forming reactions involving the intermediacy of alkylaromatic metallacycles [27] formed by insertion of strained alkenes into arylpalladium bonds, followed by aromatic metallation (Eq. (20), L = triphenylphosphine).



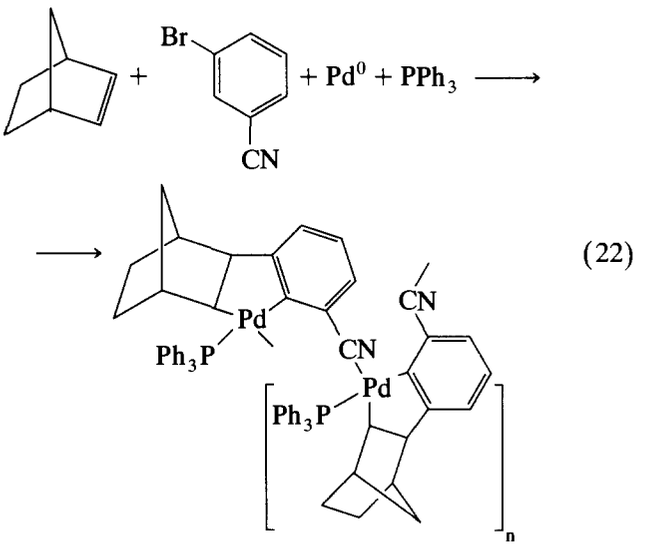
(20)

We obtained and isolated metallacycles of this kind by two methods. One is the reaction of arylnorbornylpalladium halides in the presence of a base and of heterocyclic ligands such as phenanthroline (Eq. (21)) [28].



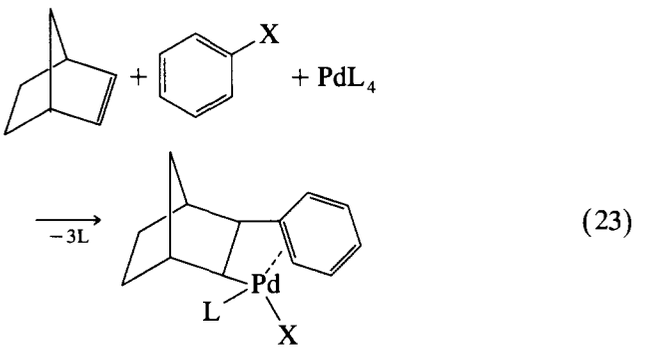
(21)

The other is reaction of 3-bromocyanobenzene with norbornene in the presence of palladium(0) and triphenylphosphine. A polymeric complex precipitates directly from the reaction solution (Eq. (22)) [29]. It can be dissolved again in pyridine.



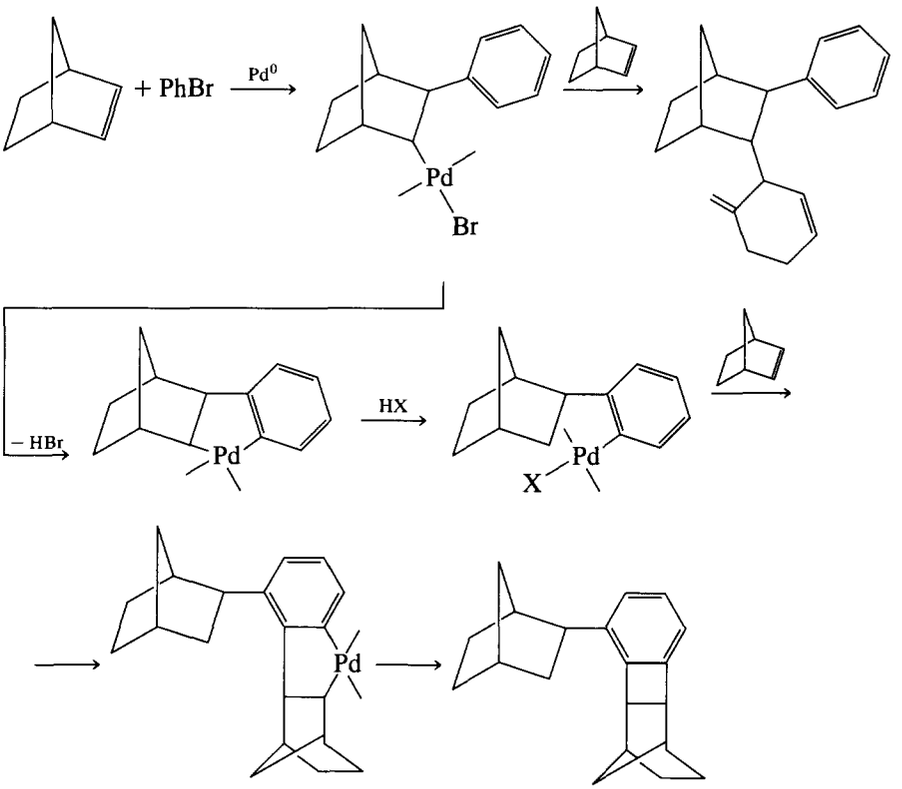
(22)

Similar alkylaromatic metallacycles were recently reported [30] (Eq. (23), X = Br or I; L = PPh_3).

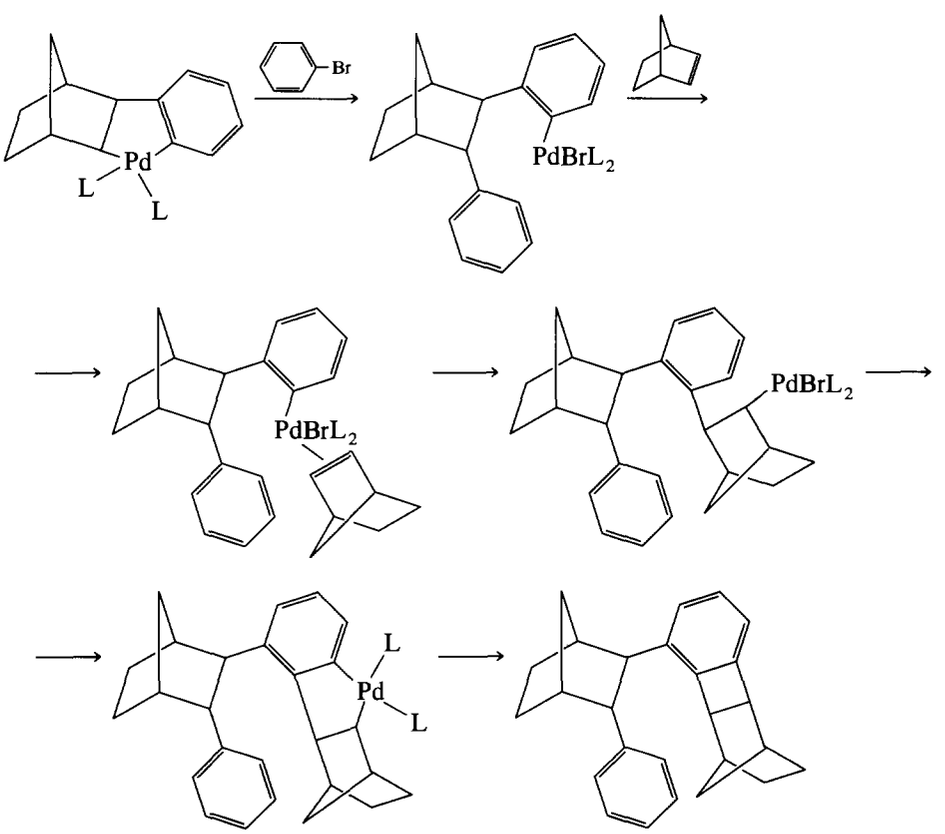


(23)

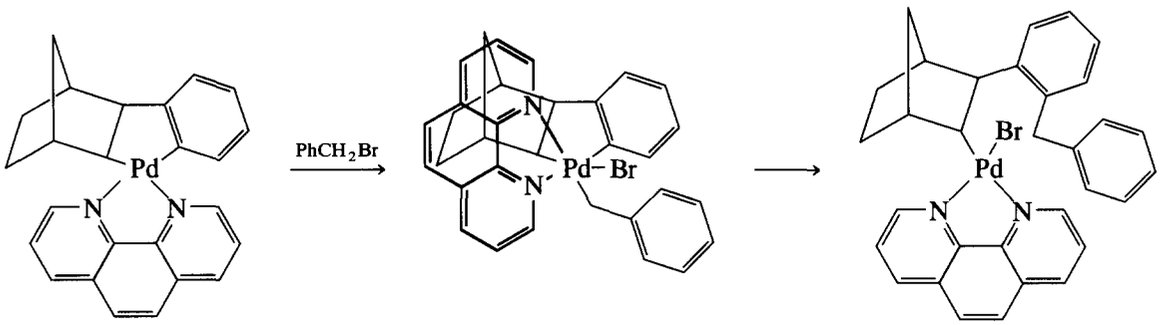
There is η^2-coordination of the aromatic ring to palladium. Further reaction with alkali metal hydroxides led to the metallacycle of Eq. (20) (L = triphenylphosphine).



Scheme 6. Alternative pathways leading to functionalization of aliphatic or aromatic moieties.



Scheme 7. Proposed pathway for the functionalization of the two ends of a palladacycle.



(24)

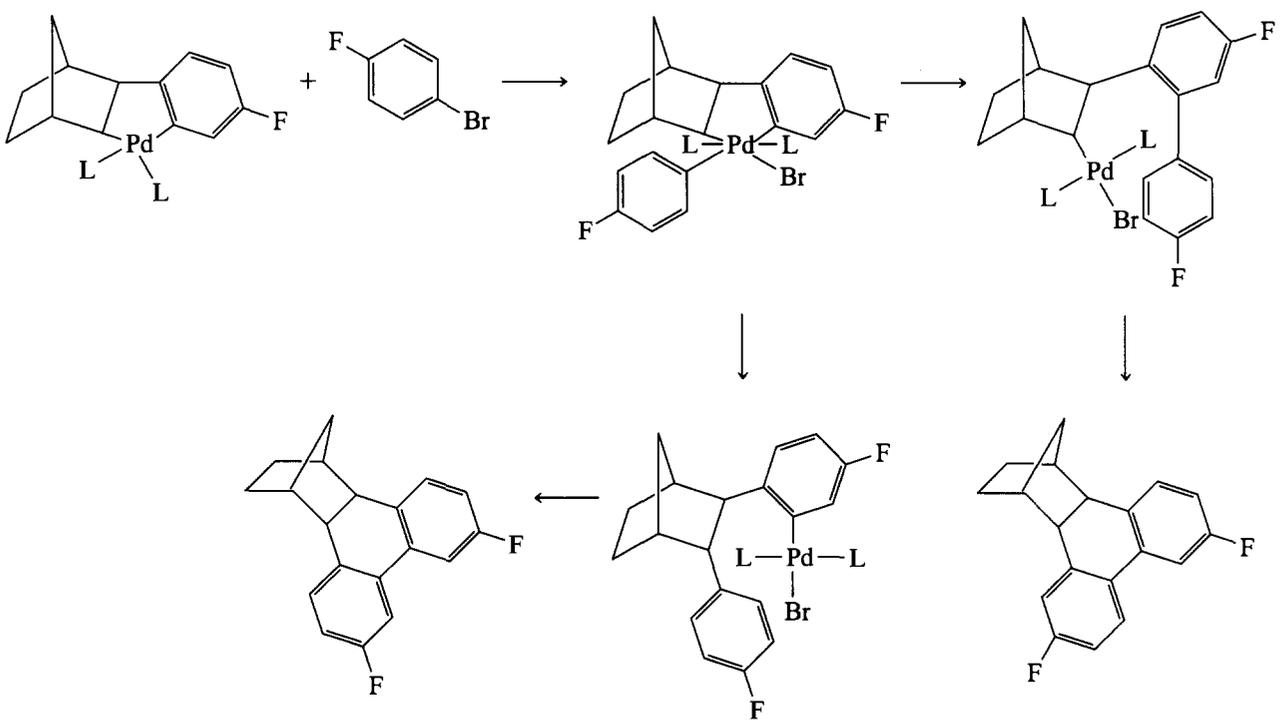
Although a rich chemistry of these metallacycles has been described [30,31], we prefer to concentrate on recent developments concerning functionalization of aromatics via oxidative addition of organic halides to palladium(II) metallacycles.

Our first observation on this subject referred to the possibility of functionalizing the aliphatic and the aromatic part of the arylnorbornylpalladium complex with norbornene (Scheme 6) [32].

The result was interpreted as involving ring opening of an intermediate palladacycle by oxidative addition of a protonic species, HX, followed by reductive elimination to give a new complex containing a palladium-to-aromatic carbon bond [27,32]. Therefore, a palladium(IV) intermediate was postulated. The hypothesis was confirmed by the isolation of palladium(IV) complexes from the oxidative addition of benzyl halides to the palladium(II) metallacycle (Eq. 24) [28,33].

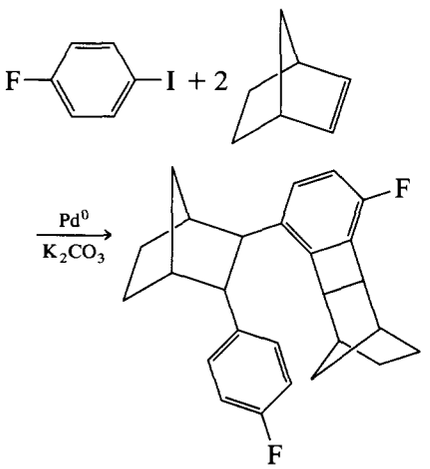
These complexes were the first in the series of alkylaromatic palladacycles to be obtained and among the few palladium(IV) complexes described in the literature [34]. The benzyl group of the complexes prepared according to Eq. (24) migrates spontaneously to the aromatic part.

With aromatic halides the corresponding palladium(IV) complexes were not isolated, but aryl migration to the norbornyl site of the metallacycle was observed. A nice selectivity of this process was achieved with 4-flu-



Scheme 8. Proposed pathway for the formation of hexahydromethanotriphenylenes via palladium(IV).

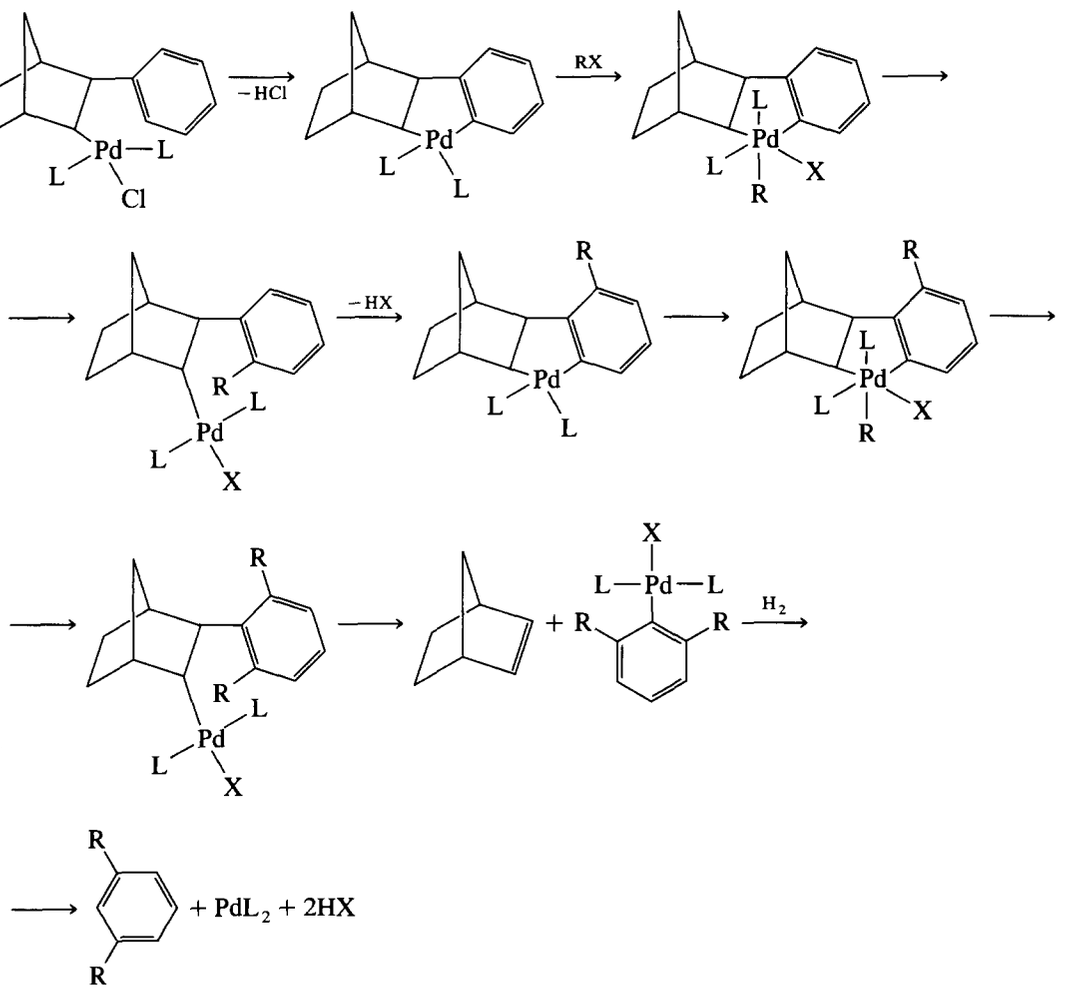
oroiodobenzene in dimethylformamide containing potassium carbonate. Whereas the 4-fluorophenyl group migrated to the aliphatic site, the palladium migrated to the aromatic site and reacted further with nozbornene. At 80°C an 81% yield was obtained, although at low conversion (26%) (Eq. (25)) [35]. The reaction proceeds according to Scheme 7 (referring to unsubstituted bromobenzene, L = dimethylformamide).



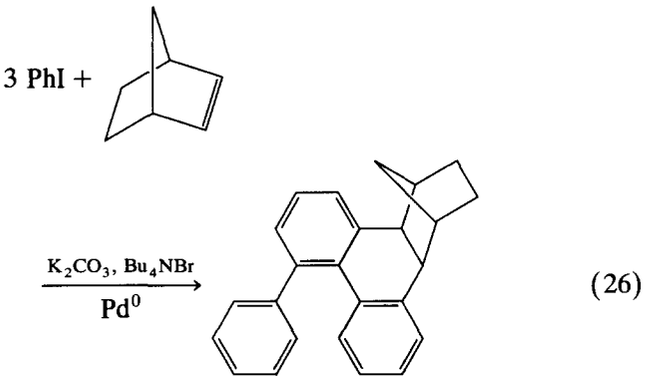
(25)

The small tendency of the phenylnorbornylphenylpalladium intermediate in Scheme 7 to close a ring between the two phenyl groups allows norbornene to compete successfully for reaction. However, ring closure to a hexahydromethanotriphenylene derivative was observed with both the intermediates (shown in Scheme 8) formed by reductive elimination from the postulated palladium(IV) intermediate) [32]. As expected with 4-fluorophenyl bromide, the norbornyl-bonded palladium complex and the aryl-bonded complex gave the hexahydromethanotriphenylene compounds in a 3 : 1 ratio (45% yield). The entire process has been interpreted as shown in Scheme 8.

Another pathway, not yet clearly defined, which could involve an aryne intermediate, is connected with the above-mentioned reluctance of the aryl-bonded palladium complex to undergo an electrophilic aromatic substitution leading to a bis-aryl-bonded palladacycle (Eq. (26)) [36].

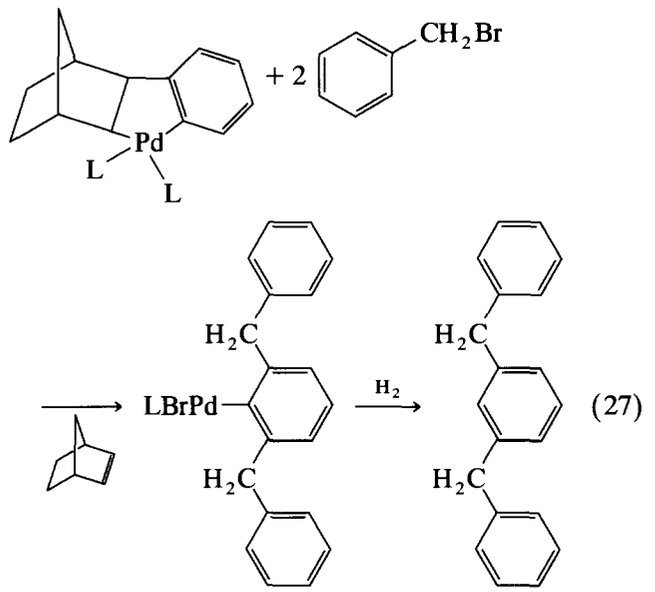


Scheme 9. Proposed pathway for selective aromatic functionalization via norbornene assistance.



(26)

An unexpected development of aromatic functionalization via palladium(IV) intermediates was found recently (Eq. (27)) [37]. Starting from phenylnorbornyl-



(27)

palladium chloride dimer in dimethylformamide as ligand and solvent, and using 4-fluorobenzyl bromide, an 87% yield of the 1,3-disubstituted benzene was obtained at room temperature.

The alkylation process of the aromatic part of the metallacycle can be effected twice in the same reaction because, after the first alkylation, there is the possibility of a new ring closure and a new oxidative addition to form a palladium(IV) complex, which undergoes reductive elimination to a complex containing two alkyl substituents in the aromatic ring. What happens then is the expulsion of norbornene, with formation of a 2,6-disubstituted arylpalladium complex. Passing dihydrogen into the solution readily leads to a 1,3-disubstituted arene (Scheme 9) [37].

As shown, the result of this multistep process is the selective formation of a 1,3-disubstituted arene. The function of norbornene in this process is to help metallacycle formation and the subsequent oxidative addition–reductive elimination steps. Once the process is complete, norbornene is removed, much as a scaffold after the construction of a building.

In conclusion, transition metal-catalysed reactions can be advantageously controlled by using substrates able to form chelates or metallacycles. These species impose strict requirements, resulting in high chemo-, regio- and stereoselectivity for reactions that would hardly be possible by conventional methods. In particular, multistep organic syntheses can be achieved with high selectivity under mild conditions.

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