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Review

THE TERMINATION STEP IN PALLADIUM-CATALYZED INSERTION REACTIONS

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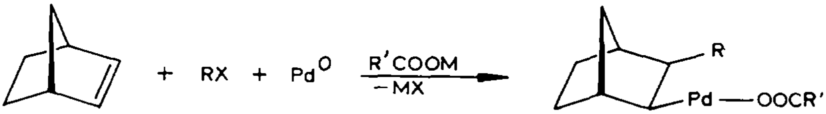
Summary

C–H activation of several types of molecules, ranging from olefins and alkynes to non-activated aliphatic and aromatic compounds, is shown to occur with the same model system, involving a norbornylpalladium bond, stable towards hydrogen elimination, in the presence of suitable molecules or groups. Alternatively, hydrogen transfer can be observed if hydrogen donors are present and nucleophilic attack following insertion of CO.

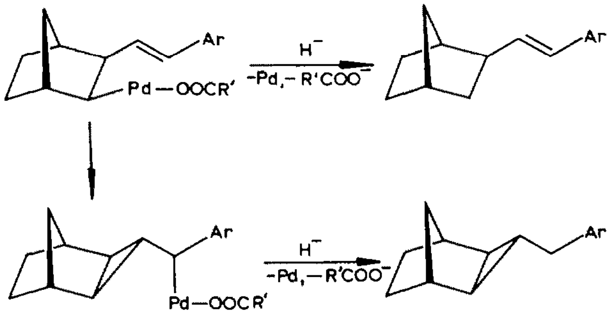
Group VIII metal complexes are efficient catalysts in a number of organic reactions, involving stepwise addition of different molecules. The metal elimination or termination step is of fundamental importance in a catalytic process because it determines the possibility of recycling the metal. Palladium chemistry is particularly interesting in this respect and we have been working out a simple model to study the different ways by which the termination process takes place. Our model is based on the formation of a palladium-carbon bond stable towards β-hydrogen elimination, which is the most common elimination pathway, by reaction of an aryl or vinyl halide RX with norbornene, palladium(0) and alkali carboxylates R'COOM (eq. 1), (non reacting ligands are omitted in this and subsequent equations).



(1)

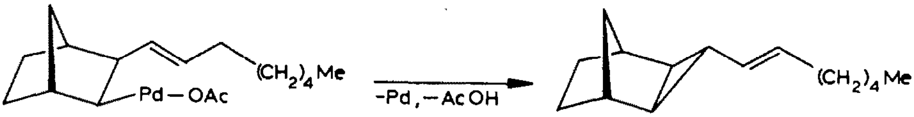
This is a very simple reaction, which takes place in organic solvents such as anisole at 60–120°C and gives *cis,exo* adducts. We then follow the behaviour of this system as the R group is varied.

Depending on the type of substituents present in the organic chain we observe different behaviour. We recently reported that styryl halides ArCH=CHX react with norbornene and hydrogen donors in presence of palladium(0) and alkali carboxylates. The complexes resulting from norbornene are rather resistant to reductive elimination, the vinyl group and the metal being *cis,exo*. Elimination occurs readily, however, by hydrogen transfer from suitable hydrogen donors such as formates, thus giving rise to a catalytic reaction. Hydrogen transfer can also occur after a new double bond insertion leading to condensed cyclopropane rings [1] (eq. 2).



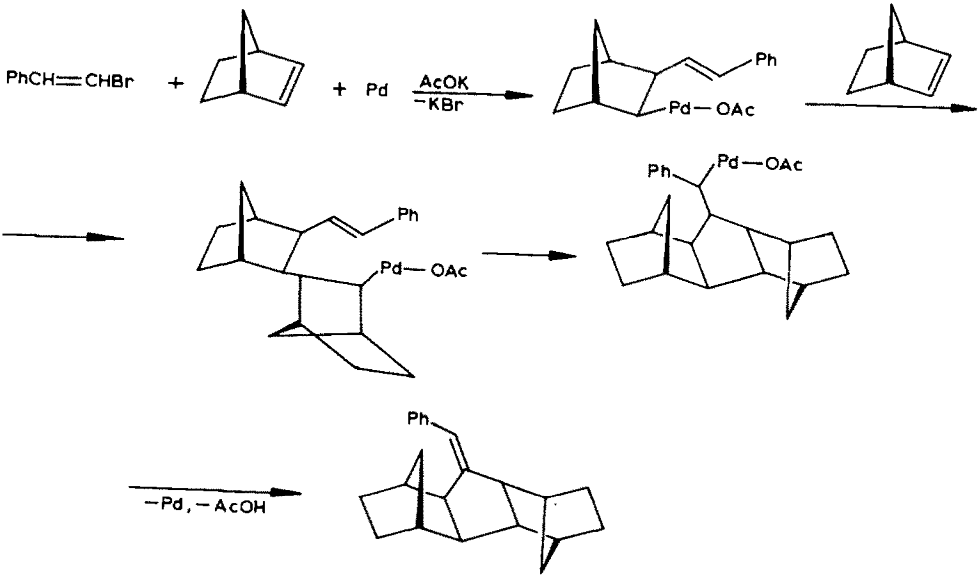
(2)

Under similar conditions (80°C) but in absence of hydrogen donors, cyclopropane rings can still be formed if a CH_2 group is present α to the vinylic double bond (with 1-bromooct-1-ene and norbornene 56% selectivity at 54% conversion of the bromide) [2] (eq. 3).



(3)

A favorable arrangement for β-hydrogen elimination from the allylic CH_2 determines the course of this reaction. If a styryl compound is used, however, this elimination cannot occur, but the system can insert a second molecule of norbor-

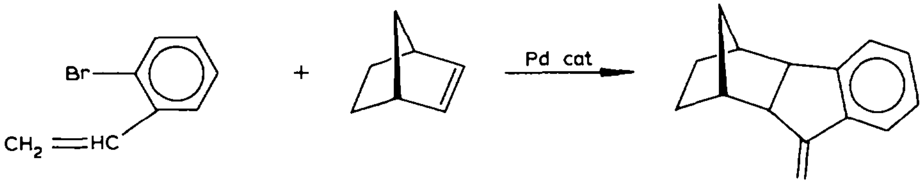


(4)

nene. After this step the situation is still the same in respect of β-hydrogen elimination, but a new addition to the styryl double bond allows termination, by elimination of a vinylic hydrogen (105°C, 74% selectivity at 89% conversion of *E*-β-styryl bromide) [3] (eq. 4):

The favorable arrangement for termination is reached only after three insertions, two of two molecules of norbornene and one of the styryl double bond. The X-ray structure shows that the product is highly symmetric as far as the five condensed cyclopentanes are concerned. The phenyl group is distorted from the cyclopentylidene plane by about 25° [3]. Only one of the possible isomers is formed, probably owing to steric hindrance in the palladium complex undergoing ring closure.

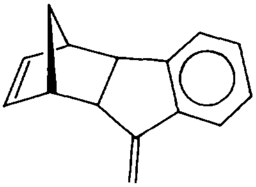
A similar concept, namely favoring elimination by placing a suitable substituent on the organic chain, has been applied to the synthesis of another condensed cyclopentane structure. We started from *o*-bromostyrene and norbornene in presence of $Pd(PPh_3)_4$. Reaction 5 took place (80°C, 75% yield on the bromide) [3]. The



(5)

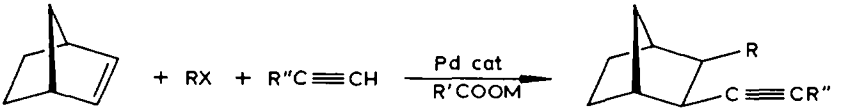
pattern is similar to the previous one, involving oxidative addition of *o*-bromostyrene to palladium(0), and consecutive norbornene and vinyl group insertions followed by H-elimination, which readily occurs from the original vinyl group.

The same reaction can be performed with norbornadiene. The attack on the double bond still is *cis,exo*. The predominant reaction involves only one of the two norbornadiene double bonds (compound I):



(I)

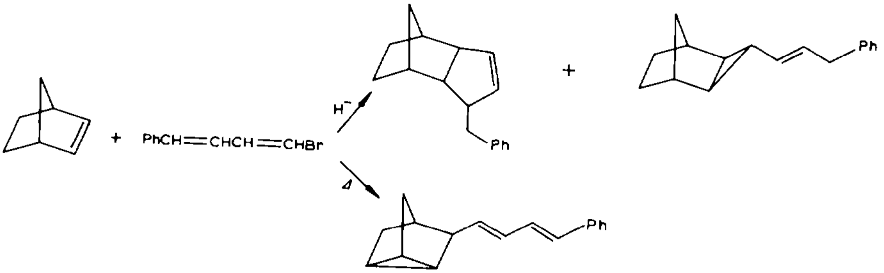
Activation of acetylenic CH in the termination step has also been observed with the same norbornene-based system [4]. When aryl and vinyl halides RX are treated with norbornene and 1-alkynes R″C≡CH on palladium(0) catalysts in presence of alkali carboxylates the following reaction takes place at ca. 80°C (eq. 6).



(6)

The type of addition still is *cis,exo*. The same stereochemistry has been observed also for norbornadiene.

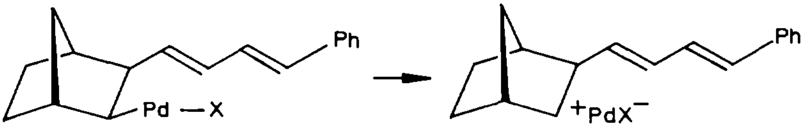
So far we have seen that allylic, olefinic and acetylenic hydrogen can be involved in the termination step. The patterns of these reactions conform to the generally accepted scheme of oxidative addition, insertion and β-hydrogen elimination. Change of the substituents, however, results in new elimination patterns. This can be illustrated for 1-*Z*-3-*E*-4-phenyl-1-bromobutadiene. The main reaction is no longer cyclopentane ring formation. This cyclization only occurs in 49% yield in the presence of a hydrogen transfer agent and is accompanied by the formation of another compound (24% yield) containing a condensed cyclopropane ring [2]. In absence of the hydrogen transfer agent another pathway, leading to tricyclene ring formation (32%), is observed (eq. 7).



(7)

Another compound formed in 24% yield corresponds to termination by the acetate ion after norbornene addition.

We can at present only speculate about the mechanistic course of the reaction leading to a tricyclene derivative. Formation of a radical, a carbene or a carbonium ion is conceivable. On the basis of the known solvolytic pathway of 2-substituted norbornanes, leading to nortricyclene, [5–7] a mechanism in which the PdX^- group is the nucleofugal species appears likely (eq. 8).

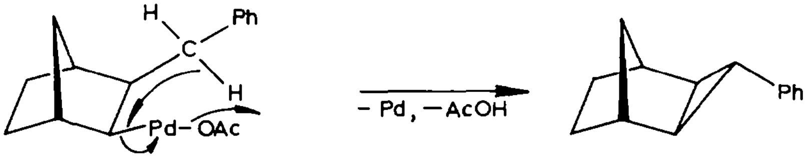


(8)

The main difficulty lies in the fact that the Pd–C bond, which is probably polarized in the direction $R^- \; PdX^+$ in the complex resulting from oxidative addition of the bromo derivative to palladium(0), must be modified by insertion of new molecules and by the influence of the other coordinated molecules or groups so as to behave as if polarized in the direction $R^+ \; PdX^-$ in certain cases, while in other cases (e.g. addition of a new molecule of norbornene or of an alkyne) the "carbanionic" character of the R group must be preserved.

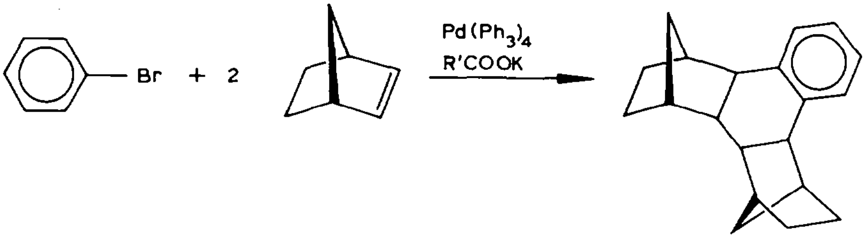
Another group which prefers the mechanism observed for the phenylbutadienyl group is benzyl [2]. Reaction 9 occurs. Most of the benzyl bromide used is recovered as the acetate (52% selectivity at ca. 20% conversion of the bromide into norbornene insertion products). In this case a solvolytic pathway can again account for the product formed.

This and the previous one are catalytic reactions involving activation of saturated C–H bonds. At this point the question arose of whether a corresponding activation of aromatic C–H bonds was possible, and for R = phenyl this type of activation has, in fact been observed [8]. The main product from norbornene and bromobenzene, obtained in a yield near to 55% at 105–110°C, always with $Pd(PPh_3)_4$ as catalyst



(9)

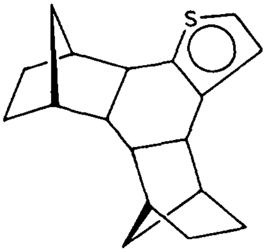
and in presence of potassium acetate, results from the reaction of two molecules of the former with one of the latter. The two norbornane rings are *trans* to each other (eq. 10).



(10)

Although there is another possible structure in which the bridging methylene groups are placed on the same side of the tetrahydronaphthalene ring, this possibility has to be discarded in view of the large steric hindrance in the palladium complex undergoing ring closure.

By this way it is possible to add a variety of substituents to the norbornane skeleton. Many products can now be prepared by very mild one-pot reactions; for example, using 2-bromothiophene in place of bromobenzene, compound II forms predominantly.



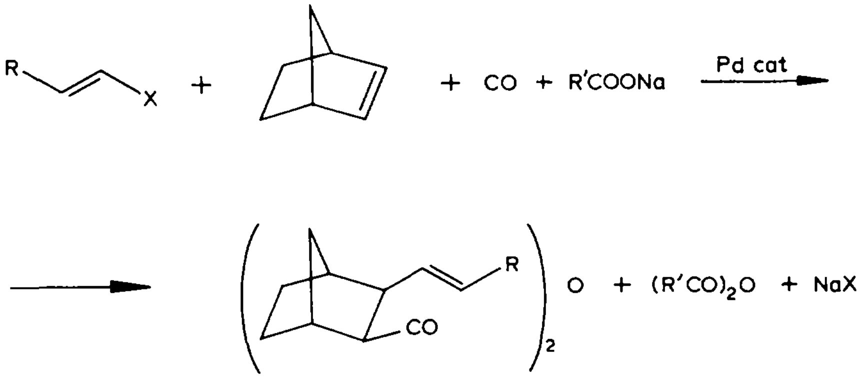
(II)

To our knowledge palladium-catalyzed activation of an aliphatic or aromatic C–H bond to form C–C bonds in the termination step of insertion reactions has not been reported before. Palladium-promoted C–H activation not involving the use of oxidants has been observed for catalytic H–D exchange reactions and for stoichiometric C–C bond forming reactions [10–13]. Catalysis can also be achieved in C–C coupling reactions if oxidants are added to the palladium complex [13–15]. In our case, however, the catalytic cycle does not require oxidants other than the organic halide which attacks the palladium complex in the termination step, thus regenerating the catalytic cycle.

C–H activation is not the only process leading to metal elimination. The termination mode strongly depends on the type of the last molecule inserted into the Pd–C bond. If CO is inserted the favored termination type is no longer hydrogen elimination but nucleophilic attack by suitable species present in the reaction medium. Thus in the case of vinyl halides, reaction with CO takes place at low temperature according to a well known pattern [16] (eq. 11), even in the presence of

$$\mathrm{RCH{=}CHX + CO + AlkOH \xrightarrow{cat} RCH{=}CHCOOAlk + HX} \qquad (11)$$

norbornene. With the system adopted here, however, involving the use of carboxylate salts at 80°C, the reaction is diverted towards insertion of norbornene, thus reaching the stage when elimination is inhibited. At this point CO can be inserted and the newly formed acylpalladium bond becomes susceptible to nucleophilic attack by the carboxylate ions present in solution, with formation of the corresponding mixed anhydrides. The species actually isolated are the separate anhydrides produced by disproportionation of the mixed species, however [17] (eq. 12).



(12)

It can be concluded that the last unit inserted largely determines the type of nucleophilic or electrophilic species involved in the termination step, no matter what the charge distribution is in the Pd–C bonds formed in the preceding steps. The model we have tested has proved to be very useful because it has enabled us to observe termination pathways not previously described.

Acknowledgement

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Note added in proof. A further termination pathway consisting of β,γ-cleavage of a C–C double bond of a norbornene ring has been recently observed. M. Catellani and G.P. Chiusoli, to be published).