# Nucleophilic Addition to π-Olefin-, π-Allyl- and σ-Alkyl-palladium Complexes. Examples of "Umpolung" by the Use of Organometallic Reagents

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The activation of organic substrates by transition metals has become very important in organic chemistry. Today, a great number of highly selective transition metal-promoted reactions are known. An important feature of the activation is that the reactivity of the organic molecule may be completely altered. For example, simple olefins such as ethene, which are fairly reactive towards electrophiles, may become electron acceptors on coordination to a metal and react with nucleophiles. A well known industrial application is the Wacker process, where ethene bound to palladium(II) is oxidized to acetaldehyde *via* nucleophilic addition of water[1] (Scheme 1).
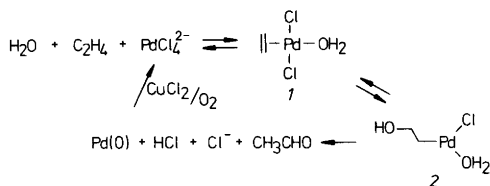
Scheme 1.

Even groups with a formal negative charge, such as π-allyl systems and carbanions may be converted into electron acceptors: These types of "umpolung" reactions may be illustrated by the formation of allylamine from allylmagnesium chloride *via* the π-allylpalladium complex *3*.[2] Also the transformation
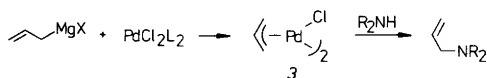
of the σ-complex *2*, formally a carbanion attached to palladium, into the chlorohydrin *4* nicely demonstrates the principle.[3]
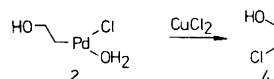
Our studies on nucleophilic addition to olefins were inspired by the Wacker process and our purpose was to develop an analogous process for amination of olefins.

In principle, the addition of nucleophiles to metal bound π-systems may take two different routes. A free nucleophile may add directly to the π-system (path (a), Scheme 2) or it may coordinate first to the metal and then be transferred internally to the π-system (path (b), Scheme 2). The stereochemical outcome of the two processes will be different in that path (a) leads to *trans* addition of the metal and the nucleophile across the π-system while path (b) results in *cis* addition.
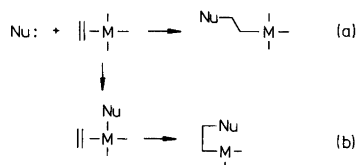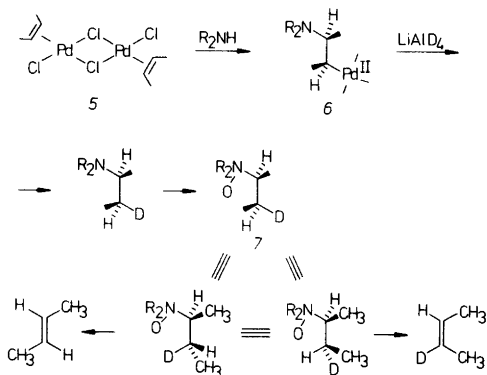
Scheme 2.

The two processes (a) and (b) will probably also show electronic differences. The process (a) would be expected to be strongly dependent on the charge

on the olefin and be accelerated by electron withdrawal from the olefin. In contrast, the reaction (b) would in general be expected to be a concerted cyclic process, which does not necessarily require any induction of charge on the olefin.

A study of the stereochemistry of palladium promoted amination revealed that this reaction proceeds *trans* according to path (a).[4] Due to the lability of the intermediate σ-complex *6*, this could not be proven directly by NMR as done for the corresponding mercury compound.[5] Instead, an indirect method was used, (Scheme 3). The *Z*-2-

Scheme 3.

butene palladium complex *5* was reacted with dimethylamine at −70 °C to give the σ-complex *6*. Addition of lithium tetradeuterioaluminate led to the displacement of palladium by deuterium with retention of configuration.[6] The alkylated amine thus formed was oxidized to the *N*-oxide *7*, which on moderate heating undergoes *cis*-Cope elimination[7] of hydroxylamine. Elimination of a hydrogen atom gives deuteriated *Z*-2-butene while elimination of a deuterium atom gives non-deuteriated *E*-2-butene. The stereospecificity of the reaction could then be determined by measuring the deuterium content in the individual isomer by mass spectrometry. The same sequence applied to *E*-2-butene gave, as expected, non-deuteriated *Z*-butene and deuteriated *E*-2-butene.[4] The total stereospecificity is >98 % if correction is made for isotope effects and a small amount of deuterium − hydrogen scrambling, which occurs in the reduction step. It thus seems safe to conclude that amination is a completely stereospecific *trans* process according to path (a), Scheme 2.
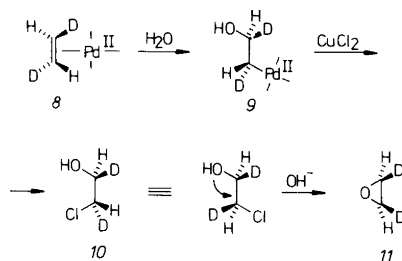
Scheme 4.

Also the Wacker reaction appears to be a *trans* process despite earlier claims to the contrary.[8] This may be shown by examining the stereochemistry of the chlorohydrin *10*, obtained from specifically deuteriated *Z*- or *E*-dideuterioethene. Chlorohydrins are frequently formed as byproducts in the Wacker reactions, and become the major product when the relative concentrations of the oxidant, copper chloride, and chloride ions are increased (Scheme 4). Reaction of *E*-1,2-dideuterioethene gives the chlorohydrin *10*, the stereochemistry of which may be accurately determined as *threo* by microwave spectroscopy. The accuracy is even better if *10* is first converted to the epoxide *11* (Scheme 4). Independent experiments show that the cleavage of palladium − carbon bonds by cupric chloride − chloride ions occurs with inversion at carbon.[10] The primary step, the addition of water, must thus be *trans* to yield the intermediate σ-complex *9*.[3] Again, the stereospecificity is essentially complete.

trans-Hydroxypalladation is also inferred from independent experiments which involve cleavage of the palladium − carbon bond of *9* by carbon monoxide.[11]

It thus appears that amines and water add preferentially as external nucleophiles according to path (a), Scheme 2. This is also true for acetate [8c,12] alcohols [13,14] and stabilized carbanions like β-diketonates.[15] In contrast, non-stabilized carbanions like methyl [16] and phenyl carbanion [17] preferentially add *cis* after coordinating to palladium (path (b)). These results appear to be of general validity and similar conclusions may be drawn from experiments with olefin complexes of platinum [18] and iron.[19]

Nucleophilic attack on π-allylpalladium complexes seems to follow the same pattern. Thus the addition of dimethylamine to the π-allyl complexes

12 a X=N(CH₃)₂
   b X=OCH₃

13 a X=Y=N(CH₃)₂
   b X=OCH₃,Y=N(CH₃)₂
   c X=OCH₃,Y=OAc
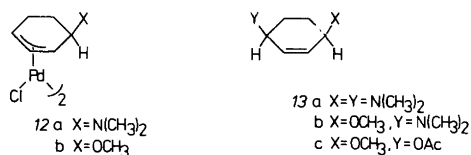
12 yields the *cis*-compounds *13*; that is, the nucleophile is added from the face of the π-allyl system opposite to palladium.[20,21] Stabilized carbanions like dialkyl malonates[22] and ketone enolates[23,24] react similarly. Acetate shows an interesting behaviour in that it may be added from either the same or the opposite face, depending on the reaction conditions. Thus in the presence of chloride, the palladium complex *12b* gives exclusively *13c* by *trans* attack where as in the absence of chloride *cis* attack occurs[25] to yield *15*.

14   15
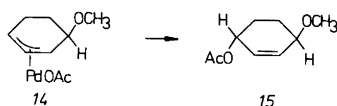
Generally however, it appears that the addition reactions follow the trend observed for π-olefin systems, that is hetero atom nucleophiles and stabilized carbanions add *trans* according to path (a) (Scheme 5) while hydride[26] and carbanions add *cis*[27] according to path (b), (Scheme 5). Again, the
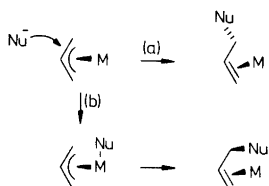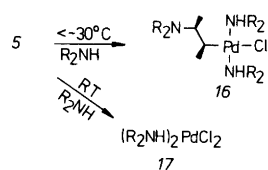
Scheme 5.

results appear to apply to complexes of other metals but palladium, *e.g.* molybdenum.[28]

The early work on amination of π-olefin-[29] and π-allylpalladium[2] systems clearly indicated the importance of cationic intermediates. For the amination of π-olefinpalladium complexes, the importance of the relative charge on the olefin and the metal is also indicated by the keen competition between amination and displacement of the olefin. At temperatures above −30 °C displacement becomes the major reaction (Scheme 6) but it may be noticed also at lower temperatures.

To explore how the formal metal oxidation state and the formal charge on an olefin complex might

5 $\xrightarrow[R_2NH]{<-30°C}$ 16

$\downarrow$ RT, R₂NH

(R₂NH)₂PdCl₂
17

Scheme 6.

effect the charge of the olefin, *ab initio* calculations were performed on a number of model nickel-olefin complexes.[30] As might be expected, the calculations show the metal to carry the major positive charge in the complexes. Thus, from purely electrostatic considerations, the metal would be expected to be the major target for nucleophiles. However, the calculations also indicate that the formal charge of the complexes will have an important effect on the relative metal − olefin charge. In the neutral complex *18* the olefin is essentially neutral and the

18   19

metal charge +0.9. In the positively charged complex *19* the nickel charge is increased slightly to +1.1 while the olefin charge is strongly increased to +0.4. The nucleophilic attack on the olefin would thus be expected to be much more favoured in the charged complex *19*.

The fact that three equivalents of amine per palladium are required to complete the amination reaction[29] suggests two reasonable pathways (Scheme 7). In both, the first equivalent serves to generate a mono nuclear complex *20*. In path (a) the second equivalent generates a charged species *21*, which then − in the true amination step − reacts with the third equivalent of amine to yield a σ-complex *22*. Alternatively, path (b), a σ-complex *23* could form directly from *20* by nucleophilic attack

20   21

23   22
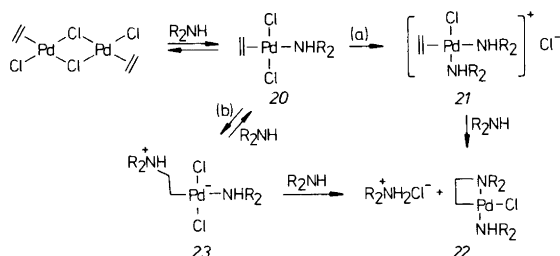
Scheme 7.

by the second equivalent of amine. The function of the third equivalent would then simply be to drive the equilibrium by deprotonating the complex 23.

In path (a) the ion pair 21 is formed and should be detectable by conductivity measurements. In contrast, in path (b) the only ionic species formed at any concentration is amine hydrochloride, which is essentially insoluble under the conditions used for the experiments (dimethylamine, THF solution).

The addition of dimethylamine to 1-decene and 1-butene palladium complexes did give rise to a moderate conductivity, but, surprisingly, a maximum conductivity was obtained at an amine − palladium ratio of 1:1 instead of 2:1 as would result from the formation of the complex 21 in path (a).[31] The most reasonable explanation is that an alternative ion pair 24 is formed, perhaps in rapid

equilibrium with the mono-nuclear complex 20 as indicated by NMR. NMR also reveals that nucleophilic attack on the cationic part of the complex yields the σ-complex 22. Compatible with all our data (conductometric titrations, quench studies, ^{1}H- and ^{13}C NMR studies) is the concomittant formation of a fairly insoluble ion pair 25. This is converted back to 24 in the presence of free amine (Scheme 8).[31]

Indirect support for the mechanism in Scheme 8 is obtained from studies on π-allyl systems. When π-crotylpalladium chloride is treated with N,N,N',N'-tetramethylethylenediamine (TMEDA) in THF solution, the conductivity reaches its maximum at an amine − palladium ratio of 1:2 (Fig. 1). This corresponds to the formation of the ion pair 27, which may be well characterized by NMR at temperatures below − 40 °C. For the related ion pair from π-allylpalladium chloride, the definite structure has been established by X-ray crystallography.[32]
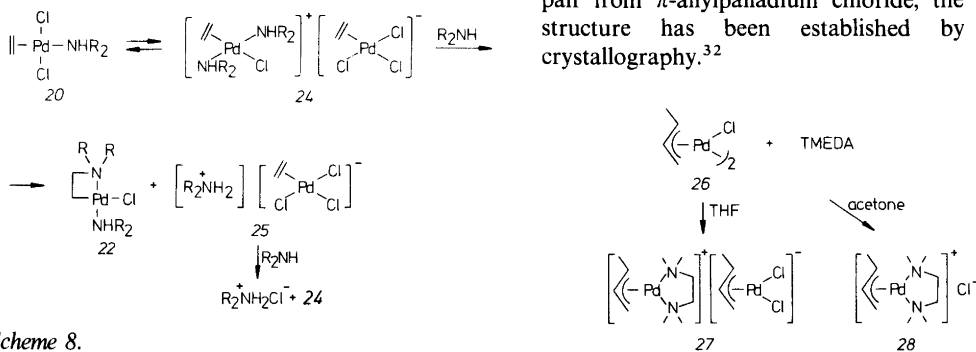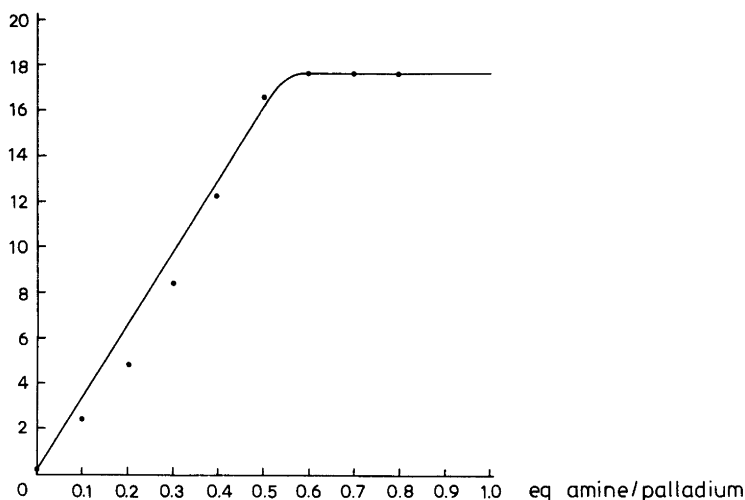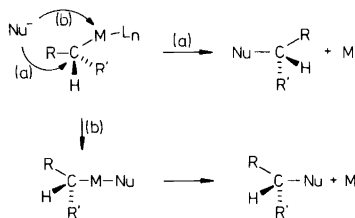
Scheme 8.

Fig. 1. π-Crotylpalladium chloride and N-tetramethylethylenediamine in THF solution.

It is interesting to note that at $+40\,°C$, the exchange of the π-allyl group between the negative and positive halves of 27 becomes rapid relative the NMR time scale. The exact mechanism for this exchange, which appears important also for the olefin complexes[31] is not clear, but an intramolecular exchange of the π-allyl group between the two halves of the ion pair is the most attractive[33] possibility.

The formation of the ion pair serves to illustrate the importance of the solvent in reactions of π-allyl-palladium complexes and similar systems. For instance, in acetone, π-crotylpalladium chloride and TMEDA give the simple ion pair 28 instead of 27.

The importance of charge is evident also for the reactions between σ-alkylmetals and nucleophiles. Both nucleophilic substitution[3,10,34] (path (a), Scheme 9) and reductive elimination[35] (path (b), Scheme 9) are promoted by added electron acceptors. Furthermore, stereochemical studies,[3,4,6,25,34,36] which make it possible to distinguish between the two pathways, indicate a similarity between π- and σ-metal systems in their reactions with nucleophiles. Also with σ-alkyl systems external attack is preferred by hetero atom nucleophiles[3,4,34] (path (a)), while carbanions and hydride generally coordinate and then react by reductive elimination[4,6,36] (path (b), Scheme 9).

Scheme 9.

It is interesting to note that the nucleophiles that react according to path (a) may be classified[37] as hard bases and those reacting according to path (b) as soft bases.

In addition to charge, orbital interactions are clearly important in the reactions of π-olefin,[38] π-allyl[39] as well as σ-alkyl[40] metal complexes. Other important factors are the relative oxidation potentials of the reacting ligands in combination with the ability of heteroatom ligands to stabilize charge by using their lone pair electrons.[40e] This idea may be illustrated for alkylmetals in the
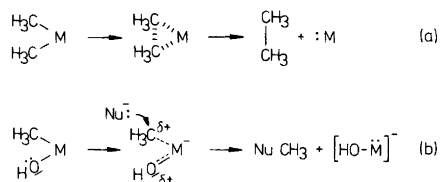
Scheme 10.

following way: Reductive elimination may be regarded as a concerted, gradual oxidation of two coordinated methyl carbanions to two methyl radicals which couple to ethane (Scheme 10, path (a)). In contrast, the decomposition of methyl-metal hydroxide may take a different route (path (b), Scheme 10) because the methyl carbanion will be more readily oxidized than the hydroxyl group.[40e] Interestingly, it should also quite readily acquire carbonium ion character on account of its higher polarizability.[37] The oxygen will presumably also interact with an electron demanding metal atom, but probably by forming a metal – oxygen double bond rather than by loss of electron density from the metal – oxygen σ-bond. It is conceivable that migration of this strongly coordinated hydroxyl group to the coordinated positive methyl group is less favoured than attack by external nucleophile, as observed experimentally.[3,10,34]

This is also in accord with the principle of hard and soft acid and bases (HSAB) in that the more polarizable soft ligand e.g. alkyl, aryl and hydride will more readily undergo reductive elimination and also in an unsymmetrical case acquire positive charge.

It is not obvious how these ideas apply to π-olefin and π-allylmetals, but it should be born in mind that a π-olefin metal complex may also be regarded as a 3-membered metallacycle.

Synthetic applications. Although a major part of our work has been devoted to mechanistic studies, we have also been concerned with synthetic transformations *via* nucleophilic additions to π-olefin and π-allylpalladium complexes. The σ-complex 29, obtained from aminopalladation of an olefin, may be transformed into a number of functionalized derivatives (Scheme 11). Reduction with hydrogen or hydride gives amine,[29] oxidation with lead tetraacetate gives acetoxyamines,[34b,41] while the use of other oxidants such as bromine or *m*-chloroperbenzoic acid produces diamines[42] and aziridines.[43] The reactions are highly stereospecific
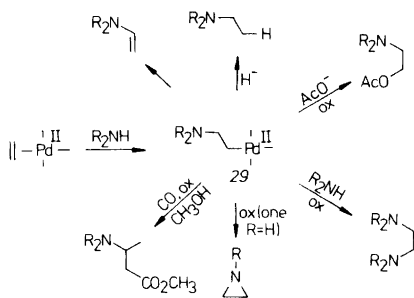
Scheme 11.

and permit the *cis*-addition of two functional groups to a double bond. The oxyamination reaction has been used to prepare a number of aminoalcohols of pharmaceutical interest, *e.g.* 30 and 31.[41,44] By the use of optically active chiral ligands or nucleophiles an asymmetric induction was obtained in the oxyamination reaction *e.g.* *trans*-2-butene→32.[45] Also the use of a chiral ligand in the analogous palladium-promoted alkylation of 1-hexene resulted in an enantiomeric excess of up to 32% in the alkylated product.[46]
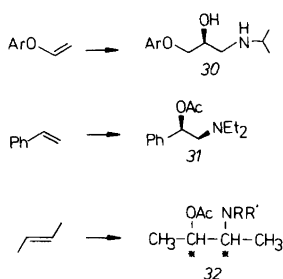
Reaction of the compound 29, finally, with carbon monoxide and an oxidant gave derivatives of β-aminoacids.[47] In analogy to the Wacker process, catalytic amination of olefins to yield enamines should be possible. Unfortunately, the expected enamines are not stable under the reaction conditions, but readily oxidized by palladium(II).[48] Only in special cases, therefore, has catalytic amination of double bonds been achieved *e.g.* 33→34.[49]
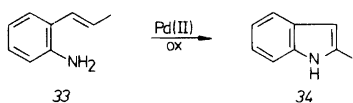
Also the work on nucleophilic additions to π-allyl systems has produced some results that may be of use in synthesis. Amines are readily added to π-allylpalladium complexes.[2] The reaction is stereospecific[20] and the regiochemistry may be controlled by the added ligands.[33] For instance, treatment of the π-allylpalladium chloride complex 36 with dimethylamine in the presence of more than three equivalents of triphenylphosphine produces selectively the allylamine 37. In contrast, the reaction of the charged complex 36b (BF$_4$⁻ is essentially non-coordinating) with dimethylamine in the presence of 1 to 2 equivalents of phosphine produces exclusively the isomeric allylamine 35 (Scheme 12).
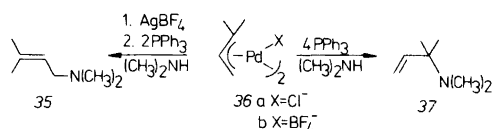
Scheme 12.

The amination of the π-allyl complexes is stoichiometric but a catalytic reaction, proceeding *via* π-allyl complexes, is possible if palladium(0) is used as catalyst and allylic acetates as substrates.[50] Allyl acetates are versatile synthetic intermediates and the palladium-catalyzed displacement of the acetoxy group by stabilized carbanions such as sodium diethyl malonate has been extensively used in organic synthesis during recent years.[51]

Catalytic telomerizations of 1,3-dienes *via* π-allyl metal complexes is also possible using palladium(0) and nickel(0) catalysts. These transformations proceed *via* bis-π-allyl-metal complexes 38 (Scheme 13). A number of different nucleophiles may be utilized *e.g.* acetate, dialkylmalonates and amines.[51b,52] The mechanism

Scheme 13.

of the reaction is not completely understood but in the amination reactions using nickel catalysis, the formation of a charged intermediate *39* is indicated.[53] By the use of this reactions, selective nickel catalyzed formation of bisoctadienyl methylamine *41* is possible.[53,54] If the palladium(0) catalyzed reaction of butadiene is performed in the presence of *e.g.* allyldimethylamine, the latter will participate in the reaction. Thus oxidative addition of the allylic amine to palladium(0), followed by an exchange reaction of the π-allyl complex formed with *38*, would give complex *42*. Selective carbon−carbon and carbon−nitrogen bond formation would explain the formation of the branched amine *43a*, which may be thermally rearranged to the linear amine *43b*.[54]

42

If palladium(II) is used as catalyst or promotor 1,3-dienes may also be difunctionalized. A number of different groups x and y may be added *e.g.* alkoxide,[21] acetate,[25,55] amine,[20,21] dialkyl malonate,[56] enolates[23] and chloride[58] (Scheme 14).

X,Y = Cl ,CH₃O, AcO, R₂N, (RO₂C)₂CH.
RCOCH₂, RO₂CCH₂

Scheme 14.

In analogy with difunctionalization of simple olefins, the two groups are generally stereospecifically introduced *cis* in cyclic dienes (for an exception giving *trans*, see below). The *cis*-stereochemistry is a result of two *trans*-additions. Most of these reactions are stoichiometric but recently stereoselective catalytic processes for 1,4-acetoxychlorination[57] and 1,4-diacetoxylation[25] of 1,3-dienes have been developed. For instance, butadiene, isoprene and 1,3-cyclohexadiene were converted to *46, 47* and *48*, respectively, in ≥70% yield.[57] The 1,4-diacetoxyla-

46   *47*   *48*

tion reaction showed a remarkable dual stereoselectivity in that *cis*-acetate (*e.g. 49*), was obtained as expected when chloride ions were present, but

49   *50*

in their absence, the *trans*-diacetate (*e.g. 50*) could be selectively obtained[25] (*cf.* the formation of *13c* and *15*).

The ability of transition metals to selectively activate organic substrates and allow specific transformations has had a strong influence on organic chemistry during the last decade. Today a great number of regio- and stereoselective reactions are known that are promoted or catalyzed by transition metals.

In this brief review we have tried to present some ideas and results on mechanistic pathways in the reactions of π-olefin-, π-allyl- and σ-alkylpalladium complexes. We have also given a few examples of how these reactions may be applied to organic transformations. It is our hope that the results presented demonstrate the usefulness of a mechanistic approach in the development of organic reactions catalyzed by transition metals.

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