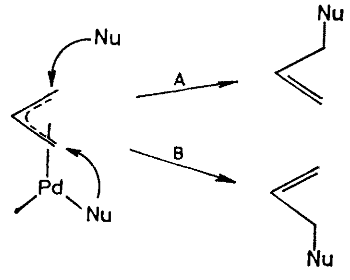
Stereochemistry of Nucleophilic Attack on π-Allylpalladium Complexes. Evidence for *cis*-Migration of Acetate from Palladium to Carbon

By JAN-E. BÄCKVALL,* RUTH E. NORDBERG, EVA E. BJÖRKMAN, and CHRISTINA MOBERG
(*Department of Organic Chemistry, Royal Institute of Technology,* S-100 44 *Stockholm, Sweden*)

Summary Formation of 4-methoxycyclohex-2-enyl acetate (**3**) from the π-allylpalladium complex (**2**) shows that the acetate has attacked the π-allyl ligand from the same side as the metal (*cis*-addition).

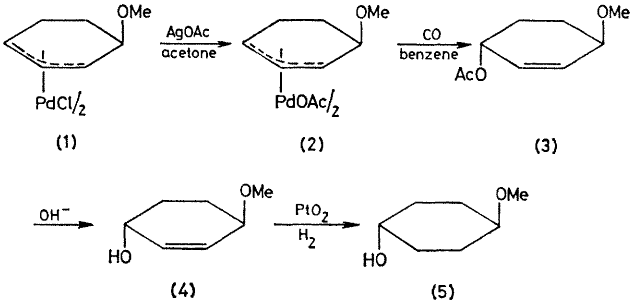
THE stereochemistry of nucleophilic addition to π-allyl- and π-olefin-palladium complexes has been investigated extensively during the last decade.[1–8] The two principal modes of addition to π-allyl complexes are shown in Scheme 1.

Recently Trost *et al.*[2,3] found that $Pd(PPh_3)_4$ catalyses the *cis–trans* isomerization of substituted cyclohexen-3-yl acetates. They rationalized the isomerization by assuming the formation of a π-allylpalladium intermediate, which may give both *trans*-and *cis*-acetate addition (paths A and B, respectively). A comparison of nucleophilic attack on π-olefin-, π-allyl-, and σ-alkyl-palladium complexes suggests[4] that *cis*-migration is preferred only by nucleophiles such as aryl, methyl, and hydride, whereas *trans*-attack is favoured by heteronucleophiles and soft carbon nucleophiles. Thus, for π-allyl complexes, dimethyl malonate[5,6] and amine[7] have been shown to add *trans* (path A) whereas hydride[8] has been shown to add *cis* (path B). We therefore sought to establish whether a *cis*-migration process is possible for acetate. Our results, presented here, show that *cis*-migration of a co-ordinated acetate to the allyl-group takes place on treatment with carbon monoxide.



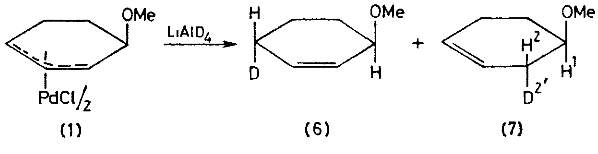
SCHEME 1

It is known that π-allylpalladium acetate complexes, on heating or on treatment with carbon monoxide, decompose to allylic acetates and palladium(0).[9] Reaction of the π-cyclohexenylpalladium complex (**1**)[10] with stoicheiometric amounts of AgOAc gave a yellow complex (**2**) which is less stable than (**1**). Treatment of (**2**) with CO in benzene gave an immediate precipitation of palladium black, with formation of the allylic acetate (**3**) (yield 70%). The ^1H n.m.r. spectrum of (**3**) (WP 200) shows sharp singlets for the methoxy- and acetoxy-groups, indicating that (**3**) is diastereoisomerically pure (>95%). The *trans*-configuration of the substituents in (**3**) was established by hydrolysis to (**4**), followed by hydrogenation† (PtO_2, H_2) which gave *trans*-4-methoxycyclohexanol (**5**) (Scheme 2). The product (**5**) was identified by comparison with authentic samples of *cis*- and *trans*-4-methoxycyclohexanols.‡ The ^1H n.m.r. spectra (WP 200) of *cis*- and *trans*-(**5**) are quite different in the region δ 1·0—2·0 and furthermore the methoxy-group singlets of the two isomers have a shift difference of 0·02 p.p.m.,§ which enabled a quantitative analysis to be made [(**5**) >93% *trans*]. The *trans*-4-methoxycyclohexanol was also identified by its toluene-*p*-sulphonate.[11,12] Thus the formation of *trans*-(**3**) from (**1**) shows that the attack by acetate has occurred from the same side as the metal (path B).



SCHEME 2

The π-allylpalladium complex (**1**), prepared from cyclohexadiene, has previously been assumed to have a *trans*-configuration on the basis of a *trans*-methoxypalladation[13] of one of the double bonds and its n.m.r. spectrum.[14] In order to establish the *trans*-configuration of the starting π-allylpalladium complex beyond doubt, (**1**) was reduced with $LiAlD_4$ in tetrahydrofuran at -75 °C [equation (1)].



(1)

Palladium(0) was immediately precipitated to give the methoxy[$^2H_1$]cyclohexenes (**6**) and (**7**), identified by g.l.c., m.s., and n.m.r. spectroscopy. The *trans*-configuration of H^1 and H^2 in (**7**) follows from the vicinal coupling constant

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† For a similar hydrogenation see ref. 7a.

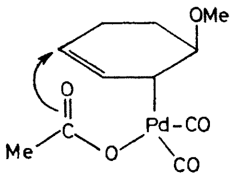
‡ (a) Prepared by the hydrogenation of *p*-methoxyphenol with 5% rhodium–alumina catalyst, giving a mixture of *cis*- and *trans*-(**5**) (ref. 11). The *cis*- and *trans*-4-methoxycyclohexanols were separated according to E. L. Eliel and T. J. Brett, *J. Org. Chem.*, 1963, **28**, 1923.

§ The chemical shifts for the methoxy-protons are (WP 200, $CDCl_3$): δ 3·32 [*cis*-(**5**)] and 3·34 [*trans*-(**5**)].

$J_{1,2}$ 7·0 Hz ($CDCl_3$),[15] as determined by spin-decoupling and observing H^1 Since the hydride ($LiAlH_4$) is known[8] to cleave the allyl–palladium bond with retention of the configuration at carbon (*cf* path B), the *trans*-configuration of deuterium and the methoxy-group in (**7**) shows that the π-allyl complex (**1**) has the *trans*-configuration

To our knowledge this is the first established example where a heteronucleophile migrates from palladium to an unsaturated carbon ligand, such as allyl or olefin, in a *cis*-addition process The acetate migration may occur either directly in the π-allyl complex or, more likely, after rearrangement to a σ-allyl complex (**8**), which would resemble an S_N2' substitution (S_N2' substitutions often occur with *syn*-stereospecificity[16])

It has recently been claimed[3,7b] that amines can also add *cis* (path B) as well as *trans* (path A) to π-allylpalladium complexes This was based on the fact that the palladium(0)-catalysed amination of *cis*- and *trans*-3-acetoxy-5-methoxycarbonylcyclohex-1-ene in each case gives a *cis*-*trans* mixture of amine product (path A: path B 1·9: 1)



(8)

We have never observed any significant contribution of *cis*-attack by amines [7a] and when (**1**) was treated with an amine, external attack by the amine occurred (path A: path B *ca* 20: 1) [17]

We thank the Swedish Natural Science Research Council and "Stiftelsen Bengt Lundqvists Minne" for financial support

(*Received, 9th June* 1980, *Com.* 617)

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