COMPETITIVE PALLADIUM-PROMOTED AMINATION OF BUTENES

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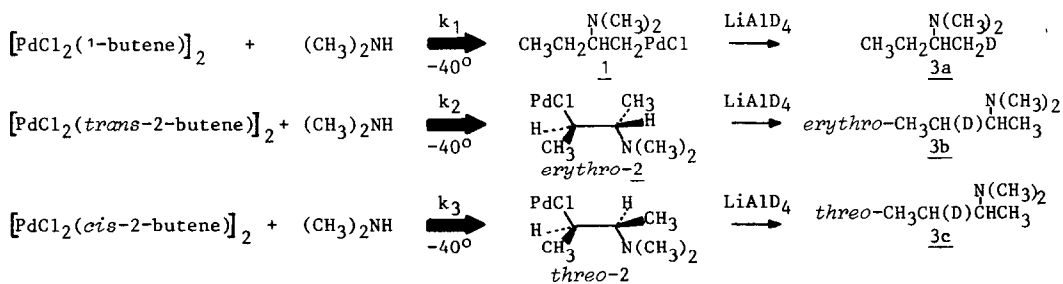
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In a recent study we have shown that palladium(II) promotes rapid amination of simple olefins.[1]   Palladium and the amine are added *trans*[2] to the olefin, forming a σ-complex, which can be isolated at low temperature.[1,3]   It was found that *trans*-olefins reacted more readily than the corresponding *cis*-olefins, as indicated by product yields. Although this is contrary to what is generally found for *trans*-addition reactions,[4] similar findings have been reported for the Wacker process.[5]   In closely related reactions like methoxypalladation[6] and amino-mercuration,[7] which proceed *trans*, *cis*-olefins react faster than *trans*-olefins.   In fact the relative reactivity of *cis*- and *trans*-olefins in the aminopalladation reaction and the Wacker process conforms rather well with that observed for cycloaddition reactions.[8]

Since product yields only give a qualitative estimate of rates and might be unreliable, we decided to investigate the relative rates of amination for the three *n*-butenes. The relative rates were found to decrease as follows: 1-butene > *trans*-2-butene > *cis*-2-butene.

In order to ensure constant olefin concentration, the amination was performed with a large excess (≈ 25 fold) of a 1:1 mixture of two butenes. The butene mixture in THF was added to bis-benzonitrilepalladium dichloride, followed by an approximately tenfold excess of dimethyl amine.   The σ-complexes 1 and/or 2 obtained in this way were reduced *in situ* with LiAlD$_4$ to replace palladium with deuterium with retention of configuration at carbon.[2,7,9]   In this way

$[\text{PdCl}_2(\text{1-butene})]_2$ + $(\text{CH}_3)_2\text{NH}$ $\xrightarrow[-40°]{k_1}$ $\underset{1}{\text{CH}_3\text{CH}_2\overset{\text{N(CH}_3)_2}{\text{CH}}\text{CH}_2\text{PdCl}}$ $\xrightarrow{\text{LiAlD}_4}$ $\underset{3a}{\text{CH}_3\text{CH}_2\overset{\text{N(CH}_3)_2}{\text{CH}}\text{CH}_2\text{D}}$

$[\text{PdCl}_2(\textit{trans}\text{-2-butene})]_2$ + $(\text{CH}_3)_2\text{NH}$ $\xrightarrow[-40°]{k_2}$ $\underset{\textit{erythro}\text{-}2}{\text{PdCl} \quad \text{CH}_3}$ $\xrightarrow{\text{LiAlD}_4}$ $\underset{3b}{\textit{erythro}\text{-CH}_3\text{CH(D)}\overset{\text{N(CH}_3)_2}{\text{CH}}\text{CH}_3}$

$[\text{PdCl}_2(\textit{cis}\text{-2-butene})]_2$ + $(\text{CH}_3)_2\text{NH}$ $\xrightarrow[-40°]{k_3}$ $\underset{\textit{threo}\text{-}2}{\text{PdCl} \quad \text{H}}$ $\xrightarrow{\text{LiAlD}_4}$ $\underset{3c}{\textit{threo}\text{-CH}_3\text{CH(D)}\overset{\text{N(CH}_3)_2}{\text{CH}}\text{CH}_3}$

1-butene gave N,N-dimethyl-2-butylamine[10] deuterated in the 1-position (3a), while cis- and

trans-2-butene gave the amine deuterated in the 3-position (3c, 3b). The relative rates of

amination of 1:1 mixtures of 1-butene and either cis- or trans-2-butene could thus be obtained

by mass spectrometric determination of the relative yields of 1- and 3-deuterated N,N-dimethyl-

2-butylamine. This was done by measuring the two ratios M-16/M-15 (loss of CH_2D and CH_3) and

M-29/M-30 (loss of C_2H_5 and C_2H_4D) which were equal as required.[11] As a cross-check the amina-

tion-reduction sequence was also applied to a 1:1 mixture of cis- and trans-2-butene. Since the

amination is highly stereospecific proceeding trans,[2] the relative rates in these experiments

could be established by determining the relative amounts of erythro- and threo-3-deutereoamine

(3b:3c) formed using a known[2,7] method involving conversion to olefines.

The yield ratios of amine obtained in this way were 3a:3b = 6.1:1, 3a:3c = 10.9:1 and

3b:3c = 1.5:1. These figures do not directly afford the relative rates of the amination step,

since the species aminated is most certainly an olefin palladium complex. The relative con-

centration of these complexes in the presence of a mixture of olefins will depend on the

coordinative ability of the olefin.

Experiments with 1- and 2-pentenes have recently shown that the order of stability for

palladium(II) complexes is cis-2-pentene > 1-pentene > trans-2-pentene.[12] It was also suggested

that the bridged bis-olefin-dipalladium tetrachloride is the main species in solution. In order

to gain an estimate of the relative concentrations of the different olefin complexes during the

amination, the relative ability of the butenes to form palladium complexes was determined.[13]

In accordance with the results from n-pentenes the relative order of thermodynamic stability

was found to be cis-2-butene > 1-butene > trans-2-butene. Values of the relative affinity are

given in Table 1. Using these data and assuming that the complex formation is fast relative to

amination, the relative rates of amination could be determined and are given in Table 1.

The relative rates for the three n-butenes are 1:0.38:0.021 (1:trans:cis).

TABLE 1

Butene mixture 1:1	Rel. amount amine from corresponding olefin[a]	Composition of $(PdCl_2(olefin))_2$	Rel. rate of amination
1-butene:trans-2-butene	6.1 : 1	2.3 : 1	1 : 0.38
1-butene:cis-2-butene	10.9 : 1	1 : 4.9	1 : 0.019
trans-2-butene:cis-2-butene	1.5 : 1	1 : 11.2	1 : 0.06[b]

a. Mean value of three experiments (estimated errors 6.1 ± 0.4, 10.9 ± 0.5 and 1.5 ± 0.1)
b. 0.38 : 0.019 gives 1 : 0.05 (from 1-butene : trans-2-butene and 1-butene : cis-2-butene)

The higher reactivity of *trans*-2-butene over *cis*-2-butene by ≃ 18:1 is unusual, since

the *cis* isomer is generally the more reactive. In a few pertinent examples presented in Ref. 4,

ratios for *cis:trans* of 1.3 - 4.4 are given. A qualitative examination of the thermodynamic

situation is instructive. *cis*-2-Butene has about 0.7 kcal mol^{-1} higher energy than *trans*-2-

butene.[14] This energy difference should be essentially preserved during *trans*-addition, since

the product $\underline{5}$ from the *cis*-olefin for steric reasons has higher energy (up to 0.8 kcal) than the

product $\underline{4}$ from the *trans*-olefin.[15] The experi-

mentally observed higher rates for *cis*-olefins

cannot thus be explained by these considerations.

Since the energy differences are quite small a

slight relative stabilization of the *cis*-tran-

sition state might perhaps be involved (Fig. 1a).
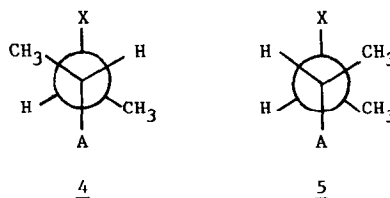
On complexing with a metal the situation is changed. In this case, the free energy of

the *cis*-2-butene palladium complex is *lower* than that of *trans*-2-butene.[16] As a result, the

relative reaction rates will depend on whether the transition state is "reactant-like" (Fig. 1b)

or "product-like" (Fig. 1c). If the transition state is product-like its energy in the addition

to *cis*-olefin should be equal or higher than in the case of the *trans*-olefin. As a result addi-
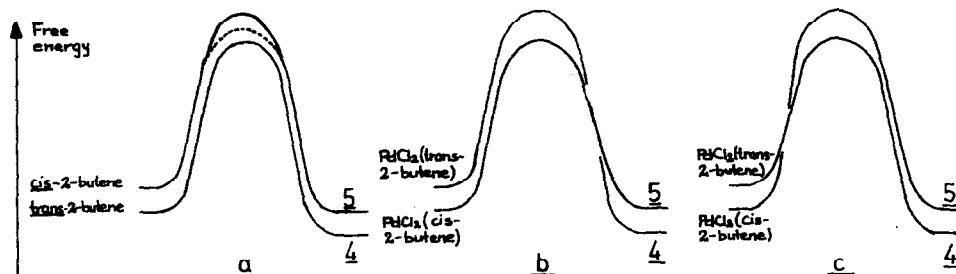

Fig. 1. (a) Addition to uncomplexed olefin; (b,c) Addition to complexed olefin.

tion to *trans*-olefin will be considerably faster, as observed for aminopalladation. On the

other hand, if the transition state is reactant-like, its energy till be lower for the *cis*-

olefin than for the *trans*-olefin. If this difference is sufficiently large, the *cis*-olefin will

react faster. This appears to be the case in methoxypalladation.[6] It is interesting to note

that the palladium-promoted hydroxylation of olefins (the Wacker process) shows a reactivity

pattern[5] similar to the aminopalladation reaction (*trans*-2-butene:*cis*-2-butene = 1:0.47 for

hydroxypalladation; 1:0.055 for aminopalladation). On rather complex kinetic grounds the

hydroxylation has been suggested to be a cyclic *cis*-addition,[5] but our results suggest indirectly

that hydroxylation is a *trans*-addition as has also been suggested by other workers.[6]

Mechanisms of additions to olefins are often based upon the observed relative reaction rates of different olefins. Our results indicate that if metal complex formation is involved, the stability of the π-olefin complexes may strongly affect the relative rates. Mechanistic assignments based on relative rates should therefore be done with great cautiousness.

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10. A small fraction of anti-Markownikoff adduct (1/7) was formed, which was corrected for (*cf*. Ref. 1).

11. (a) Correction was made for a small fraction of non-deuterated amine ($\simeq$ 1 %) and for natural abundance of ^{13}C. Blanks were also run for control; (b) Mass spectra were run at 17 eV.

12. G.F. Pregaglia, F. Conti, and B. Minasso, *J. Organometal. Chem.*, 47, 165 (1973)

13. The appropriate olefin mixture ($\simeq$ 25 excess) was stirred with bis-benzonitrilepalladium dichloride in THF at 0° for 10 min. The mixture was then cooled to −40°, left for 5 min., and transferred (with a syringe) into an excess of *n*-pentan (cooled to −40°). The precipitate was left for 3 min. and then collected by filtration. Expulsion of the butenes by 1,5-cyclooctadiene gave a butene mixture, which was collected under vacuum in a trap at −196°. This butene mixture was analysed by GLC.

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15. (a) The energy difference depends on the *gauche* methyl interaction in 5. This corresponds to approximately 0.8 kcal mol^{-1} as determined for *n*-butane;[15b] (b) D.W. Aksnes and P. Albriktsen, *Acta Chem. Scand.*, 26, 3021 (1972).

16. A calculation based on the olefin −Pd(II) equilibria (Table 1) gives $\simeq$ 0.5-0.6 kcal lower energy for the *cis*-2-butene complex.