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STEREOSPECIFIC PALLADIUM(II)-LEAD(IV)-PROMOTED OXYAMINATION OF OLEFINS

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Stereospecific cleavage of carbon-transition metal σ-bonds has recently received considerable attention. Halogen cleavage of the metal-carbon bond may occur with either inversion[1-3] or retention[3-6] of configuration at carbon. In metal-for-metal exchange reactions, retention at carbon seems to be the rule[6-9] although inversion has been observed[10] in the exchange of sterically hindered alkylcobalt(I) compounds with mercuric chloride.

It has been suggested[11] that a metal-for-metal exchange reaction occurs between palladium and lead, when lead tetraacetate is present in the olefin arylation reaction shown in Fig. 1. Alkyl transfer to lead from the intermediate alkylpalladium compound, followed by reductive elimination would explain the formation of the saturated 2-phenylethyl acetate.

Fig. 1

$$ArHgX \xrightarrow[CH_2=CH_2]{Pd(OAc)_2} ArCH_2CH_2PdOAc \xrightarrow{Pb(OAc)_4} ArCH_2CH_2Pb(OAc)_3 \longrightarrow ArCH_2CH_2OAc$$

In connection with other exchange reactions[8] and in view of the possibility of preparing β-aminoalcohols from aminopalladation adducts, it was of interest to study the reaction of palladium-carbon bonds with lead tetraacetate.

The β-aminoalkylpalladium compound 1 was prepared *in situ* at -40° by amination[12] of the appropriate olefin. The addition proceeds with *trans* stereochemistry[13] and gives diastereoisomeric σ-palladium complexes when both R_1 and R_2 differ from hydrogen. Treatment of 1 with lead tetraacetate gave an aminoacetate 2, which on subsequent hydrolysis or $LiAlH_4$-reduction was transformed

$$\begin{matrix} R_1CH{=}CHR_2 \\ | \\ Cl\text{-}Pd\text{-}Cl \end{matrix} \xrightarrow{Me_2NH} \begin{matrix} NMe_2 \; PdCl \\ R_1CH - CHR_2 \\ \mathbf{1} \end{matrix} \xrightarrow{Pb(OAc)_4} \begin{matrix} NMe_2 \; OR_3 \\ R_1CH - CHR_2 \\ \mathbf{2}\ R_3{=}Ac,\ \mathbf{3}\ R_3{=}H \end{matrix}$$

to the desired β-aminoalcohol 3. Results from some oxyamination reactions, given in Table 1, show that terminal olefins give high yields of β-aminoalcohol, whereas yields from internal olefins are moderate. This parallels yields found for the aminopalladation reaction[12] and shows that the cleavage of the palladium-carbon bond by lead tetraacetate is essentially quantitative.

The cleavage of the palladium-carbon bond by lead tetraacetate was highly stereospecific.

TABLE 1

Olefin	Product[a]	Yield %[b,c]
1-Butene	Dimethylaminobutanol (1:7.3) (3a)	84
1-Hexene	Dimethylaminohexanol (1:4.9) (3b)	77[d]
1-Decene	Dimethylaminodecanol (1:4.8) (3c)	69[d]
trans-2-Butene	*threo*-3-Dimethylamino-2-butanol (3d)	58
cis-2-Butene	*erythro*-3-Dimethylamino-2-butanol (3d)	26

a. Figures in parenthesis refer to the ratio 2-alcohol:1-alcohol as determined by glc
b. Determined by glc c. Based upon the amount of palladium used d. Isolated as the acetate

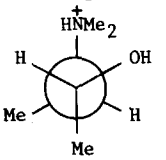
Thus, when *erythro*-1d, prepared *in situ* by aminopalladation of *trans*-2-butene, was treated with lead tetraacetate in THF, *threo*-2d was formed exclusively, and subsequently transformed[14] to the alcohol *threo*-3d. The product (3d) obtained from *erythro*-1d was identical with the product obtained from the nucleophilic ring opening[15] of *cis*-2-butene oxide by dimethylamine. *Erythro*-3d, prepared by dimethylaminolysis of *trans*-2-butene oxide, and *threo*-3d had different retention time

erythro-1d *threo*-2d *threo*-3d

on gas chromatographical analysis and the two isomers gave different nmr spectra.[16] The same sequence could be used to transform *threo*-1d into *erythro*-3-dimethylamino-2-butanol (*erythro*-3d), strongly indicating that the cleavage of the palladium-carbon bond by lead tetraacetate with replacement of palladium by acetate proceeds with inversion of configuration at carbon.

The nmr spectrum of the protonated form of *threo*-3d (Fig. 2), isolated from the reaction of *erythro*-1d, showed a coupling constant J_{23} = 9.9 Hz, which according to the Karplus equation[17] is consistent with the *threo*-isomer possessing mainly the conformation 4. No *erythro*-isomer could be detected by nmr methods.

Fig. 2



4

J_{23} = 9.9 Hz (in D_2O with acetate as counter ion)

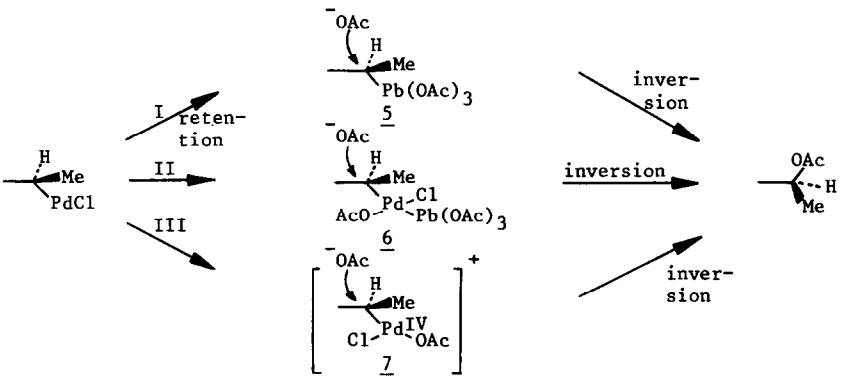
Secondary palladium-carbon bonds appeared to react faster with lead tetraacetate than primary palladium-carbon bonds,[18] to give an alkyl acetate. This indicates some carbonium ion character at the carbon during the reaction.

When an excess of amine was used in the reaction of β-aminoalkylpalladium compounds with lead tetraacetate, 1,2-diamines were sometimes formed. Thus, 1-decene gave a 60 % yield of 1,2-bis-(dimethylamino)decane when an excess of dimethylamine was used in the reaction sequence.

Three different mechanisms are considered for the palladium-carbon bond cleavage by lead tetraacetate and are shown in Scheme 1. Exchange of lead for palladium with retention of configu-

ration at carbon, followed by nucleophilic attack of an acetate ion on the alkyllead intermediate 5, would give an acetate of the observed configuration (eq. I). Of course, alkyl transfer with inversion followed by reductive elimination with retention would give the same result but seems less probable. Another mechanism (eq. II) might involve oxidative addition of lead tetraacetate

Scheme 1



to palladium, giving 6. Nucleophilic displacement of palladium would then give the acetate. A third possibility is that lead tetraacetate oxidizes palladium(II) to palladium(IV) (eq. III).

Henry[19] observed that *cis*-1,2-diacetates were formed from cyclohexene on treatment with palladium acetate in the presence of cupric chloride. He suggested that transfer of electrons from the palladium-carbon bond to copper should facilitate a nucleophilic displacement of palladium(II) (*cf.* mechanism in eq. II). A similar mechanism was also suggested for the cleavage of a palladium-carbon bond in a sequence of reaction steps rationalizing the formation of 2,6-di-*endo*-diacetoxy- and 2-*endo*-acetoxy-6-*exo*-chlorobicyclo(3,3,0)octane when 1,5-cyclooctadiene was treated with lead tetraacetate in the presence of palladium(II).[20]

Although the mechanisms II and III cannot be excluded the mechanism I involving an alkyl transfer from palladium to lead appears to be the most probable. An analogous alkyl transfer from mercury to lead is known to take place.[21] For example, treatment of arylmercury trifluoroacetate with lead tetrakistrifluoroacetate rapidly gave aryllead tristrifluoroacetate. Reductive elimination of lead(II) from the latter compound to give an aryl trifluoroacetate was favoured by electron-donating substituents in the para-position.[21a] Furthermore, organolead(IV) compounds have been shown to be stable enough to preserve configuration at the α-carbon.[22] Nucleophilic displacement of lead in such compounds has also been suggested to take place.[22b] Finally, the observation that secondary palladium-carbon bonds react more easily to give the acetate is consistent with an intermediate σ-lead compound.

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