Stereochemistry of the Alkyl Transfer from Mercury to Palladium

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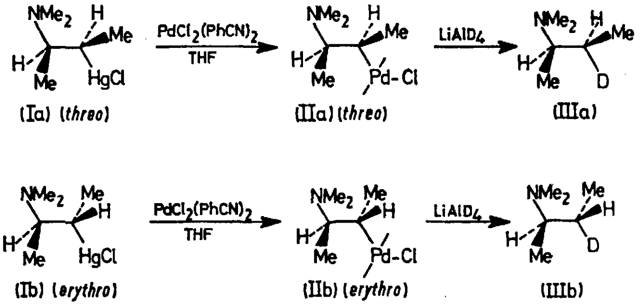
Summary Alkyl transfer from mercury to palladium has been shown to proceed with retention of configuration of the alkyl ligand by the reaction of *threo*- and *erythro*-MeCH(NMe$_2$)CH(HgCl)Me (I) with bisbenzonitrilepalladium chloride, followed by deuteriation and degradation of the product amines to olefins.

Alkyl–metal compounds frequently participate in metal-for-metal exchange reactions. The stereochemistry at the carbon atom that migrates in the exchange process provides valuable information on the mechanism of these reactions. Owing to experimental difficulties, relatively few studies have been reported on exchange reactions involving transition metals. These include alkyl migration from cobalt to mercury, which proceeds with inversion,[1] from palladium to mercury,[2] and from iron to mercury[3] which proceed with retention of configuration at the carbon atom. The transfer of a vinyl group from mercury to palladium may also proceed with retention.[4] Since the transfer of alkyl and aryl groups from mercury to palladium is of synthetic importance,[5] it was of interest to investigate the stereochemistry of this reaction. We report here an example of alkyl migration from mercury to palladium which proceeds with retention of configuration at the carbon atom.

The two diastereoisomeric mercury compounds (Ia) and (Ib) prepared by aminomercuration of *cis*- and *trans*-but-2-ene as described earlier,[6] were treated with a slight excess of bisbenzonitrilepalladium chloride in tetrahydrofuran solution at −30 to −40 °C. The palladium complexes (IIa) and (IIb) prepared in this way were treated *in situ* with LiAlD$_4$ to replace palladium with deuterium with retention of configuration at carbon.[7,8] The configurations of the resulting deuteriated amines were determined by a known method[6,8a] in which the amines are converted into olefins. The *threo*-isomer (Ia) gave *threo*-3-deuterio-*NN*-dimethylbutane-2-amine (IIIa) whilst the *erythro* isomer (Ib) gave the *erythro*-amine (IIIb) with $>90\%$ stereospecificity in both cases. A small amount of deuterium scrambling was observed, indicating that palladium migrates to some extent in the intermediates (IIa) and (IIb) *via* β-elimination and re-addition of palladium hydride. This process probably accounts for the slight loss of stereospecificity observed. Consequently the cleavage of the mercury–carbon bond by palladium(II) is completely stereospecific and proceeds with retention fo configuration which is consistent with either an S_E2(cyclic) or an S_E2-



(open)Ret reaction.[9] This conforms with other types of electrophilic reactions of the mercury-carbon bond,[10] *e.g.*, mercury-for-mercury exchange[11] and bromination[12] (in polar solvents), which have been shown to proceed with retention of configuration at the carbon atom.

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[7] Although there is only indirect evidence that simple alkylpalladium compounds are reduced with retention by $LiAlD_4$,[8a] hydride cleavage of norbornylpalladium compounds by $NaBD_4$ occurs with retention at carbon.[8b,8c]

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