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Stereocontrolled Trans and Cis Nucleophilic Attack by Acetate on π-Allylpalladium Complexes. Applications to Stereoselective Palladium-Catalyzed 1,4-Diacetoxylation of Cyclic 1,3-Dienes

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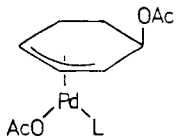
The control of stereochemistry in nucleophilic additions to unsaturated hydrocarbons coordinated to a metal is of great importance in organic synthesis.[1] Much work has been devoted to the stereochemistry of nucleophilic additions to π-allyl- and π-olefinpalladium complexes[2-7] and applications of such reactions is stereoselective organic transformations.[1b,7-10] Although both cis and trans attack by acetate on π-allylpalladium complexes appears to take place,[2,3] there are so far no methods for selecting the stereochemistry of nucleophilic attack, e.g., turning an external trans attack into an intramolecular cis attack for a given nucleophile. We recently reported that cis migration of acetate from palladium to carbon takes place in π-allylpalladium acetate complexes on treatment with carbon monoxide.[3] We have now found a very simple way of controlling the stereochemistry of nucleophilic attack by acetate on π-allylpalladium complexes.

It is known that palladium-catalyzed oxidation of 1,3-cyclohexadiene in acetic acid results in the formation of 1,4-diacetoxy-2-cyclohexene of undetermined stereochemistry.[11] Although a free radical chain process was suggested by the authors, a more likely mechanism is that the reaction proceeds via nucleophilic addition of acetate to an intermediate π-allylpalladium complex **1**, formed by trans acetoxypalladation of one of the double bonds.



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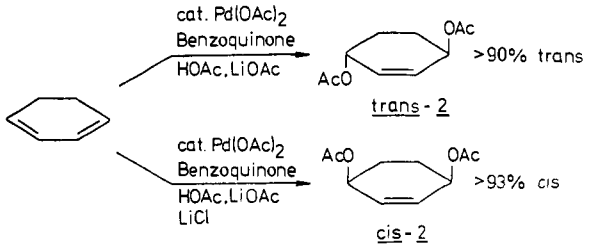
Scheme I



We have studied the stereochemistry of the 1,4-diacetoxylation and found that the presence of lithium chloride and/or lithium acetate has a profound effect on the stereochemical outcome. Oxidation of 1,3-cyclohexadiene using benzoquinone and catalytic amounts of palladium acetate in acetic acid gave a 1:1 mixture of *cis*- and *trans*-1,4-diacetoxy-2-cyclohexene (**2**). When the same oxidation was performed in the presence of lithium acetate, the main product was the *trans*-diacetate (*trans*-**2**). A remarkable change in stereochemistry was observed on the addition of small amounts of lithium chloride. Thus in the presence of both lithium acetate and lithium chloride the *cis*-diacetate (*cis*-**2**) was formed with high stereoselectivity (Scheme I). The latter reaction was more conveniently performed by using Li_2PdCl_4 as catalyst and lithium acetate as the only added salt.

The stereochemical analyses of products **2** obtained from 1,3-cyclohexadiene was accomplished by using ^1H NMR spectroscopy. The diacetates *cis*-**2** and *trans*-**2** have characteristic NMR spectra with the CH_2CH_2 grouping at 2.1 and 1.7 ppm for trans-**2** but concentrated at 1.9 ppm for *cis*-**2**.[12] Further characterization was obtained by hydrolysis of cis-**2** to the known cyclohex-2-ene-1,4-diol.[13]

In a typical procedure 1,3-cyclohexadiene (1.2 g, 15 mmol) was added during 4 h to a solution of Li_2PdCl_4 (315 mg, 1.2 mmol), LiOAc (10.2 g of the dihydrate, 100 mmol), and benzoquinone (3.0 g, 28 mmol) in acetic acid (50 mL) at 25 °C. The mixture was stirred for another 4 h at 25 °C and then filtered, diluted with brine (30 mL), and extracted with pentane. The pentane phase was washed (water, 2 M NaOH), dried ($MgSO_4$), and evaporated to give 2.02 g (68%) of essentially pure *cis*-**2** (>95% cis). Using the same procedure (only 50 mmol of LiOAc) but replacing Li_2PdCl_4 with $Pd(OAc)_2$ as catalyst gave 2.21 g (74%) of crystalline *trans*-**2** (>90% trans), mp 49–50 °C. In the same manner cyclopentadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene were oxidized to *cis*-1,4-diacetoxy-2-cyclopentene (>95% cis),[13] *cis*-1,4-diacetoxy-2-cycloheptane (>95% cis),[14] and cis-1,4-diacetoxy-2-cyclooctene (>83% cis) in 21, 57, and 41% isolated yield respectively.[15]

The change in stereochemistry found in the palladium-catalyzed oxidation of 1,3-cyclohexadiene on addition of lithium salts is best explained by a change in the mode of acetate attack on the intermediate π-allylpalladium complex **1**. To obtain more convincing evidence for such a stereocontrolled attack, we studied the stoichiometric reactions with the π-allylpalladium complex **3**,[3,16] related to the putative intermediate **1** (Scheme II). Thus treatment of complex **3b** with benzoquinone in acetic acid at room temperature resulted in cis attack by coordinated acetate to give

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(12) A quantitative analysis was possible since the signal for δ_{CHOAc} of *cis*-**2** separates from the one of trans-**2** [$(\delta_{CHOAc})_{trans}$ 5.31, $(\delta_{CHOAc})_{cis}$ 5.23 ($CDCl_3$, 200 MHz)].

(13) Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.

(14) Mp 79–80 °C. Characterized by ^1H NMR, IR, and mass spectra. ^1H NMR spectra ($CDCl_3$) for the cis and trans isomer are different. Cis isomer: δ 5.67 (s, 2, CH=CH), 5.37 (br d, J = 10.5 Hz, 2, CH-O). Trans isomer δ 5.77 (s, 2, CH=CH), 5.41 (br d, J = 6.4 Hz, 2, CH-O). Further characterization according to: Cope, A. C.; Liss, T. H.; Wood, G. W. *J. Am. Chem. Soc.* **1957**, *79*, 6287.

(15) Cyclooctadiene could also be oxidized to the *trans*-diacetate ($Pd(OAc)_2$, LiOAc) whereas the highest relative yield of *trans*-diacetate from cycloheptadiene was 50% (no lithium salts). Acyclic 1,3-dienes selectively gave 1,4-diacetate, but except for butadiene, yields were poor (isoprene, 1,3-pentadiene) due to competing Diels–Alder addition with benzoquinone.

(16) Complex **3a** is known to be of trans configuration; cf. ref 3.

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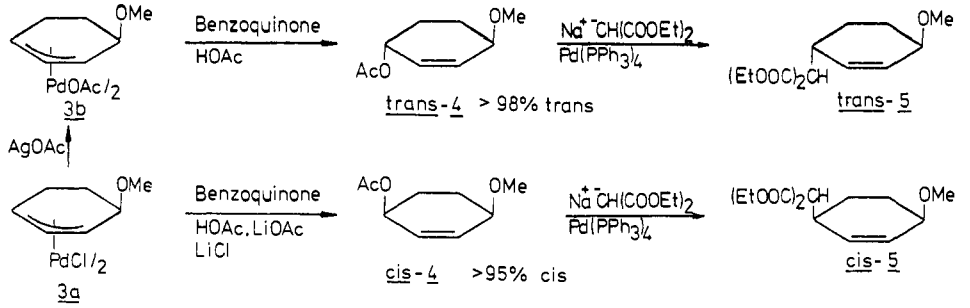
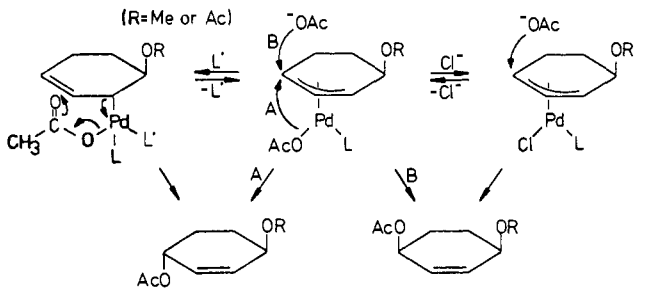
Scheme II



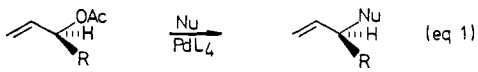
Scheme III



trans-**4** as the sole product (>98% trans). Performing the same reaction with **3b** in the presence of lithium acetate and lithium chloride changed the steric course of the nucleophilic attack and gave *trans*-**4** and *cis*-**4** in a 1:1 ratio. A clean trans attack by acetate to give pure *cis*-**4** was obtained with the chloro complex **3a**. Thus treatment of **3a** with benzoquinone in acetic acid in the presence of lithium chloride and lithium acetate gave pure *cis*-**4** with high stereoselectivity (>95% cis).[17]

A likely mechanism, which accounts for the results (Scheme III), is that chloride ions effectively block the coordination of acetate to palladium and hence hinder the cis-migration path. In the presence of chloride ligands mainly external trans attack on the π-allylpalladium complex takes place; in the absence of chloride ligands both cis and trans attack can occur depending on the acetate concentration.[18]

Since allylic acetates are versatile starting materials and can readily be stereospecifically substituted (retention) by a number of nucleophiles using a palladium(0) catalyst (eq 1),[1b,19,20] the



(eq 1)

stereocontrolled reactions reported here open a way of forming a new carbon–carbon bond or carbon–nitrogen bond with desired stereochemistry in a π-allylpalladium complex or a diene. We have demonstrated this by transforming the π-allylpalladium complex **3** into either *cis*-**5** or *trans*-**5**[21] in good yield via the corresponding acetates **4** (Scheme II).

Acknowledgment. We are grateful to the Swedish Natural Science Research Council and "Stiftelsen Bengt Lundqvists minne" for financial support and Dr. H. E. Högberg for helpful discussions.

(17) *cis*- and *trans*-**4** had different ^{1}H NMR spectra ($CDCl_3$, 200 MHz), and the cis compound was characterized with an authentic sample (cf. ref 3).

(18) Trost et al.[2] proposed a similar mechanism to explain the effect of phosphine in decreasing the Pd-catalyzed isomerization of allylic acetates.

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(21) This compound partly isomerized to the corresponding vinyl ether on prolonged reaction time. No such isomerization was observed for *cis*-**5**, indicating that a pseudoaxial proton CH–O is required for isomerization to occur. A similar isomerization of analogous compounds has recently been observed by others: Åkermark, B.; Ljungqvist, A.; Panunzio, M. *Tetrahedron Lett.* **1981**, *22*, 1055.

The Binary Metal Hydrido Anion FeH_6^{4-}: An X-ray Structural Characterization

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Since the initial studies of Weichselfelder[1] in 1926, efforts to resolve the hydridic species produced by the reaction of excess Grignard with iron(III) chloride under an atmosphere of hydrogen have met with limited success. Apparently, a complex mixture of products ranging from tan precipitates to black tars can be obtained. The breadth of results lead to the diverse conclusions that the reaction mixture contained FeH_3,[2] FeH_6,[3] $Mg(FeH_4)_2$,[4] or a variety of other hydridic products not necessarily containing iron.[5] With one possible but not probable exception,[2a] no pure hydridic product was obtained prior to the isolation of $FeH_6Mg_4X_4(THF)_8$ (X is a mixture of bromide and chloride) by one of us.[6] An X-ray structural investigation of this material was undertaken and has now revealed the presence of an unusual polyhydrido complex. We report here the results of that study and the discovery of the hexahydridoiron(II) anion FeH_6^{4-}, a new member of the very rare class of anionic binary transition-metal hydrides.

The synthesis and isolation of $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ has been reported elsewhere.[6] A yellow, air-sensitive crystal of dimensions 0.15 × 0.25 × 0.55 mm was selected for the X-ray analysis and sealed in a glass capillary under a nitrogen atmosphere. The compound crystallizes in the monoclinic space group $C2/c$ with a = 20.427 (4), b = 11.623 (2), c = 21.661 21.661 (7) Å; β = 109.39 (2)°; V = 4851 (2) Å^3; Z = 4. Two quadrants of intensity data ($2\theta < 45°$) were collected at ambient temperature

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