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## Structural Aspects of Reactive Organometallic Compounds

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**Abstract.** The structural chemistry and catalytic activity of palladium complexes with chiral or prochiral ligands and substrates has been investigated using a suite of techniques. In particular, solid-state structural characterization of complexes has provided a database from which a combination of theoretical and empirical methods are being used to parameterize the factors leading to high activity.



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many and Columbia), she completed her Habilitation in Basel in 1983 and received the *Alfred Werner Prize* of the Swiss Chemical Society in 1985. In 1996, she was promoted to Professor at the University of Basel. Further details of her research interests are to be found at <http://crystal.chemie.unibas.ch>.

Palladium-catalyzed enantioselective allylic substitutions (*Scheme 1*) constitute a highly efficient way to convert racemic starting material into optically pure products [1]. We focus on investigations of  $\eta^3$ -allyl complexes **2** with chiral phosphinoxazolines **1**, which are readily isolable, stable intermediates of the catalytic reaction cycle (*Scheme 2*) [2]. Solid-state properties of the complexes are examined by X-ray structural analysis, and the dynamic properties in solution are investigated by NMR spectroscopy [3]. It is found that  $\eta^3$ -allyl complexes usually exist as two or more rapidly interconverting diastereoisomers in solution.

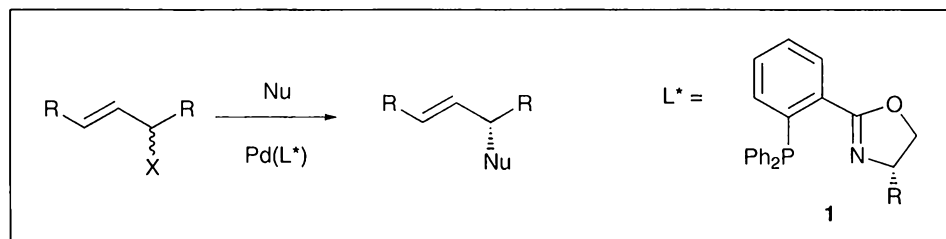
In the case of phosphinoxazoline ligands of type **1**, it is assumed that the

stereochemical outcome in the catalytic process results from nucleophilic attack at the allyl terminus *trans* to P of the main *exo*-isomer [4].

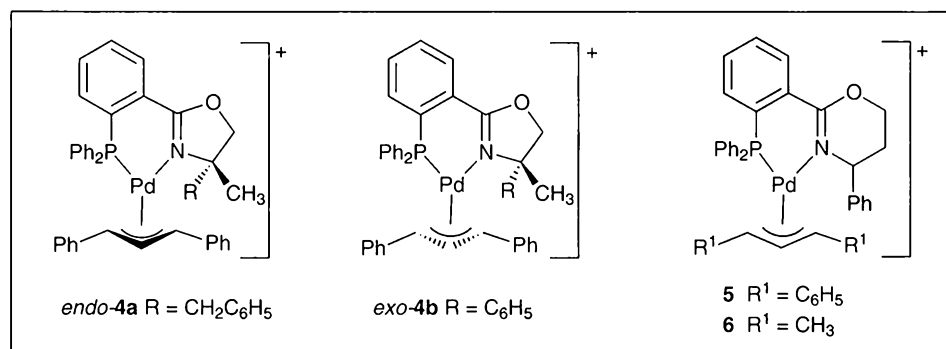
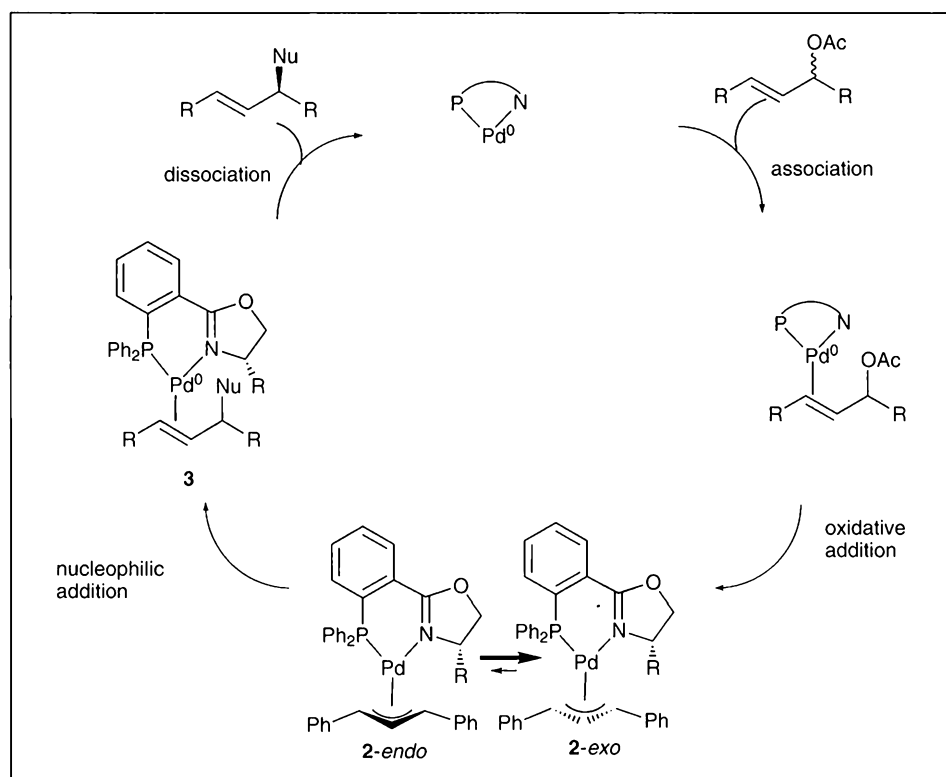
Variation of the phosphinoxazoline auxiliaries, the  $\eta^3$ -allyl system, or the metal centers gives insight into the factors which influence the relative stability and outlines the correlations between the stereochemical course of the catalytic alkyla-

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Scheme 1



Scheme 2



tion and the characteristics of the  $\eta^3$ -allyl intermediates.

The best results with chiral phosphino-oxazoline ligands in catalysis (95–99% *ee*) are found with allyl substrates bearing bulky substituents such as phenyl in the 1- and 3-positions. In more flexible systems with 1,3-dimethylallyl derivatives, the enantiomeric excess (*ee*) decreases significantly (50–70% *ee*). Investigations of 1,3-dimethylallyl complexes indicate that the decrease in enantioselectivity is connected with the formation of at least four different diastereoisomers [5].

We have concentrated our recent investigations on ligands that force the chiral information to be close to the allylic centre. Some of the palladium(II)  $\eta^3$ -allyl complexes synthesized and characterized by X-ray analysis are **4a**, **4b**, **5**, and **6**. The X-ray analysis of **4a** [6] shows that the allyl group adopts an *endo*-configuration, while all other 1,3-diphenylallyl complexes exhibit *exo*-configurations in the solid state.

The asymmetric allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate demonstrates a relationship between the orientation of the allyl

ligand and the absolute configuration of the major product. With the ligand (*S*)-**4a**, the major product has the (+)-(*R*)-configuration, in contrast to the major allylic substitution product obtained with (*S*)-**4b** and the corresponding 4-monosubstituted ligands of type **1**.

We plan to extend our investigations of palladium(0)  $\eta^2$ -olefin complexes because, whilst a lot is known about  $\pi$ -allyl complexes, only few solid-state structures of olefinic intermediates have been reported. Suitable methods for the preparation, X-ray structural and NMR characterization of these complexes have to be worked out.

A main goal of asymmetric synthesis is the design of catalytically active metal complexes and the prediction of their properties. In order to do this in a systematic manner, we hope to derive appropriate force-field parameters for the interaction of palladium with an allyl group, a phosphine and an imine nitrogen, using quantum-mechanical calculations on model systems. These theory-derived parameters will then be implemented into an established force field such as MM2. In a second step, these theory-derived parameters for the metal will be further tuned to reproduce some 50 experimental crystal structures of ( $\eta^3$ -allyl)(phosphinoaryloxazoline)palladium complexes, most of which were synthesized and solved in our group. By limiting the new force field to one class of palladium complexes, we expect – as a trade-off for restricted applicability – to achieve higher precision and better predictability within this class of structures. Further extensions to other Pd-containing complexes will depend on the success of the present project.

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