

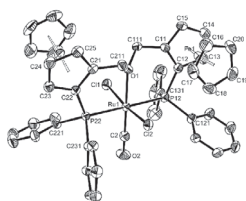
s13.m35.o2 **Design and X-ray Structures of New Chiral Ferrocenyl Ligands to be Used in Asymmetric Catalysis.**

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Keywords: Ferrocene; Catalysis; Asymetry

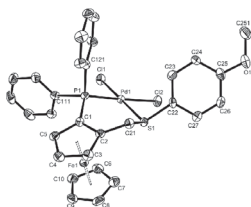
Worldwide sales of chiral drugs in single-enantiomer forms continued growing at a more than 13% annual rate. Then discovery of truly efficient methods of obtaining optically pure chiral substances remains a substantial challenge for synthetic chemists. Since the early 1970s, there is a growing interest in asymmetric catalysis. One of the most powerful general strategies is the use of chiral metal complexes as homogeneous molecular catalysts. Our group is involved in the syntheses of chiral enantiomerically pure modular ligands.

Two efficient syntheses of a chiral enantiomerically pure C₂-symmetry diphosphine-monoether will be presented. The study of the coordination chemistry of this large bite-angle diphosphine proved that this diphosphine can chelate one single metal with the two phosphorus being trans to each other.



Associated with palladium precursors, this ligand forms an efficient catalyst for asymmetric allylic substitution with good reactivity and good enantioselectivity (ee up to 81%).

Furthermore, a new family of ferrocenyl phosphine thioethers have been designed and synthesized with high efficiency. This new type of ligand proved to be efficiently bound to various metals (Pd, Pt, Ir...)



These ligands were tested in asymmetric allylic substitution, and proved to be good systems with high activity and enantioselectivity (ee up to 93%).

s13.m35.o3 **Single-Crystal-to-Single-Crystal Photochemistry in Inclusion Compounds.**

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Keywords: Photochemistry; Reactions in the solid-state; Inclusion compounds

In heterogeneous photochemical reactions, at certain extent of conversion, phase separation occurs. In contrast, homogeneous photochemical reactions are characterized by the persistence of the crystal throughout the whole conversion range. In a specific example it was shown that when the wavelength of the absorption maximum was used, heterogeneous reaction took place. However, a single-crystal-to-single-crystal photodimerization was observed when the wavelength of the flank of the absorption was chosen [1]. We have found that homogeneous reaction takes place when we irradiated inclusion compounds with a regular Xe lamp. For example, benzylideneacetophenone (a), or pyridone (c) undergo solid-state photodimerization under irradiation of its inclusion compound with (I) as the host, with no destruction the crystallinity of these compounds. The case of inclusion compound (I-c) was of special interest. At a certain stage of the reaction it became apparent that a foreign molecule was penetrating the crystal, as shown by an additional electron density that was found in the difference Fourier map, without destroying the crystal. This electron density is suspected to be the oxygen of a water molecule. Enantioselective Ring closure of (e) to (f) was observed while its inclusion compound with the chiral host compound (II) was irradiated. In all cases the effect of the geometry change, imposed on the guest molecules by the reaction, on the host molecules was severe and no damage to the crystal was observed. Therefore the crystal structures at different conversions and at the end of the reaction could be determined. In contrary to the above cases, the guest molecule tropolone methyl ether (g) in the inclusion compound with the chiral host (III) undergoes heterogeneous enantioselective photoreaction to yield (h). The disability to undergo homogeneous photoreaction is explained in terms of the space needed for this reaction.

[1] Enkelmann, V.; Wegner, G. *J. Am. Chem. Soc.* **1993**, *115*, 10390.

