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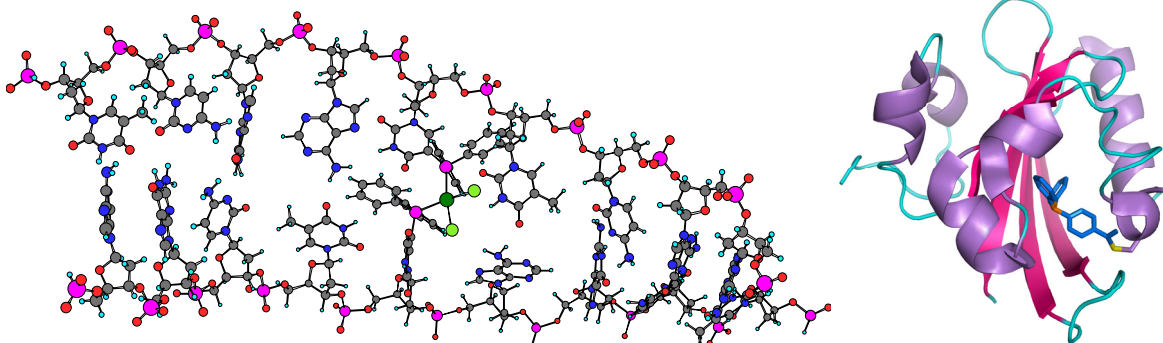
Research Interests: homogeneous catalysis, organometallic chemistry, ligand design, phosphorus chemistry, transition metalloenzymes



The main objective of our research is the development of new catalytic processes. We try to achieve this by studying the relationship between the structure of the catalyst and its performance in catalysis. Our main research interest is in the field of homogeneous catalysis with the aid of transition metal complexes and a broad range of catalytic reactions has been studied. The major activity is in the field of ligand synthesis based on phosphorus donor atoms by rational design assisted by molecular modelling. Ligand design is supported by thorough mechanistic (in-situ) studies of catalytic reactions to acquire insight in structure-activity relations. Besides the study of well-known steric and electronic ligand effects the influence of ligand geometries around the metal centre is a key issue in this research. For example, catalytic reactions can be accelerated by forcing the geometry of the “catalyst” towards a structure that resembles the transition state, as has been proposed for metalloenzymes. This has resulted in novel, very active and (enantio)selective catalysts.

A ‘de novo’ design of transition metalloenzymes

The rates and selectivity of enzymatic catalysis are seldom equalled by transition metal catalysis. Still, many important fine chemicals are produced by homogeneous catalysis because efficient enzymes for important chemical transformations like CO- and alkene insertions are lacking. By combining the concepts of biology for selective recognition with those of transition metal catalysis we develop novel, highly selective catalysts for important (asymmetric) catalytic C-C bond forming reactions. Furthermore, high substrate specificity will allow conversion of a single substrate present in complex mixtures, like those in biological systems. Several approaches are being followed. We are working on advanced systems using transition metals that contain ligands based on rigid strongly coordinating phosphines modified with relatively small oligopeptide or oligonucleotide chains. The catalytic activity of these artificial metalloenzymes or “DNAzymes” stems mainly from the transition metal part, while the selectivity of the catalytic transformation is induced by molecular recognition between the peptide chain and functionalized substrates.



Left: Computer model of PdCl₂ complex of AGCTU*AGCT self complementary duplex; U* = 5-diphenylphosphinouracil. Right: Graphical representation of Photoactive Yellow Protein modified with 4-diphenylphosphinobenzoic acid.

Selected Recent Publications

1. Activity of SPANphos rhodium dimers in methanol carbonylation. Freixa, Zoraida; Kamer, Paul C. J.; Lutz, Martin; Spek, Anthony L.; van Leeuwen, Piet W. N. M. *Angew. Chem., Int. Ed.* 2005, **44**, 4385.
2. Phenoxaphosphino-Modified Xantphos-Type Ligands in the Rhodium-Catalysed Hydroformylation of Internal and Terminal Alkenes. R. P. J. Bronger, J. P. Bermon, J. Herwig, P. C. J. Kamer, P. W. N. M. van Leeuwen *Adv. Synth. Cat.* 2004, **346**, 789.
3. In-Situ Mechanistic Studies in Rhodium Catalyzed Hydroformylation of Alkenes. Paul C. J. Kamer, Annemiek van Rooy, Gerard C. Schoemaker, and Piet W. N. M. van Leeuwen *Coord. Chem. Rev.* 2004, **248**, 2409.
4. A novel dicationic phenoxaphosphino-modified Xantphos-type ligand: Hydroformylation in Ionic Liquids. R. P. J. Bronger, S. M. Silva, P. C. J. Kamer, P. W. N. M. van Leeuwen *Dalton Trans.* 2004, 1590.
5. Dormant states of rhodium hydroformylation catalysts. Edyta Walczuk, Paul C.J. Kamer, and Piet W.N.M. van Leeuwen, *Angew. Chem. Int. Ed. Engl.* 2003, **42**, 4665.