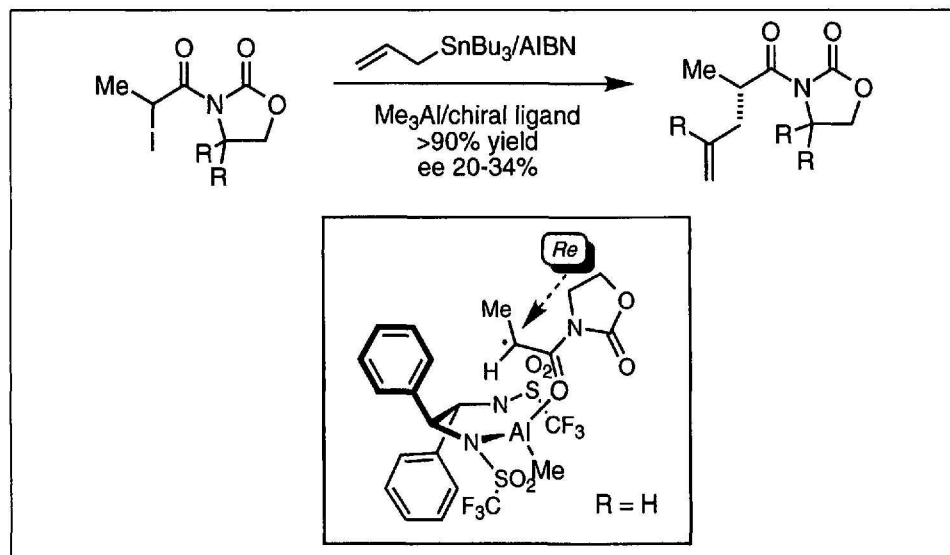


Scheme 4



in particular aluminum, for these reactions. We have also developed several different strategies for the control of the stereochemistry. Further investigation of the broad and hot topic of catalytic enantioselective radical reactions should en-

hance the range of possible applications of free-radical reactions.

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Electronic Asymmetry: Theoretical Background, Ligand Design, and Applications

Thomas R. Ward*

1. Relatives of the d^0 Bent $[\text{Cp}_2\text{ML}_3]$ Family. An Extended Hückel Molecular Orbital (eHMO) and Structure-Correlation Study of the Edge-Bridged Tetrahedron (EBT-5)

When one thinks of five coordination, the trigonal bipyramid (TB-5) and the square pyramid (SPY-5) immediately come to mind. Their interconversion, *via* the Berry mechanism, has been thoroughly studied [5]. In the field of d^0 organometallic chemistry, the bent metallocene Cp_2M fragment (Cp = cyclopentadienyl) occupies a central position. Considering cyclopentadienyls as six-electron donors occupying a single coordination site, $[\text{Cp}_2\text{ML}_3]$ com-



I was born in Fribourg on January 8th 1964 as the last of six children of John E. Ward and Ada Lovinger Ward. As an American citizen, I obtained Swiss nationality in 1976. I am married to Anouck Visinand and father of two sons, Benjamin Roald and Samuel.

After obtaining my *baccalauréat* from Collège St.-Michel in June 1983, I entered the University of Fribourg the same year as a chemistry student. I graduated in 1987 with organic chemistry as major and inorganic chemistry as minor subjects.

My interests being mostly synthetic but with a pronounced taste for group theory, I opted for a Ph.D. in organometallic chemistry at the ETH-Zürich in the group of Prof. L.M. Venanzi. The project I studied dealt with the synthesis and

coordination properties of C_3 -symmetric phosphine ligands and their use as acetalization catalysts [1][2]. This work, which was awarded the ETH Silbermedaille, benefited from a fruitful collaboration of Prof. D. Seebach as well as of Ciba-Geigy which patented our systems. I then moved to Cornell University to work under Prof. R. Hoffmann. This theoretical excursion led me into the fascinating field of heterogeneous catalysis: Why is rhodium so efficient at removing NO from car exhaust [3]? On returning to Switzerland, I joined the group of Prof. C. Floriani for a second postdoc. My main focus was the synthesis of transition-metal carbides [4]. Soon thereafter, I was awarded the Alfred Werner Fellowship and moved to Bern to undertake my independent career in Fall 1993.

I consider myself as a ligand designer fascinated by chirality. My research can be divided into three stages. After having identified a relevant problem from the current literature, I run a series of qualitative molecular orbital calculations which help me rationalize the published observations. Coincidentally, these form the basis for a synthetic project. Thus, I will describe three distinct projects at different stages of achievement: *i*) outlining a problem with the help of molecular orbital theory, *ii*) designing a ligand system, and *iii*) applications.

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plexes are five-coordinate. However, these compounds cannot be categorized as either TB-5 or SPY-5: All three ligands L are contained in the plane sandwiched between both cyclopentadienyls, but display an acute L-M-L angle ($<70^\circ$) (Fig. 1, far right). Let me call this unusual geometry Edge-Bridged Tetrahedral (EBT-5).

The catalytic properties of d^0 bent metallocenes are remarkable. I need only to mention the stereospecific α -olefin polymerization, where these catalysts are unrivalled and are the basis of a multibillion dollar market of polypropylene. Inspection of the widely accepted transition-state geometry involving a bent metallocene bound to the growing polymer and a propene reveals a $[\text{Cp}_2\text{ML}_3]$ -like arrangement, the third coordination site occupied by an agostic α -H interaction [6]. This suggested that the catalytic activity of d^0 bent metallocenes may well be due to the unusual geometry exhibited by $[\text{Cp}_2\text{ML}_3]$ complexes.

An eHMO study revealed that the EBT-5 geometry is the result of a second-order *Jahn-Teller* distortion of e' symmetry (in D_{3h}). In fact, such a distortion from TB-5 corresponds to a reverse *Berry* pathway. It is favored for all d^0 systems which contain two properly oriented strong π -donors. This model was tested with a structure-correlation analysis of all five-coordinate d^0 complexes possessing two strong π -donors. A mapping of the reverse *Berry* pathway is depicted in Fig. 1.

2. If It is not Steric, It Must be Electronic!

Until recently, most of the ligand design for enantioselective catalysis was based on steric arguments and C_2 -symmetric catalyst precursors. Eventually, electronically asymmetric bidentate P[^]N and P[^]S ligands were introduced by *Pfaltz*, *Helmchen*, and *Williams* and proved superior for the palladium-catalyzed allylic alkylation reaction, as well as for various other catalytic applications [7]. A theoretical study revealed that the pronounced *trans*-influence of P-donors was responsible for the regioselective nucleophilic attack on the terminal allyl carbon with the longest Pd-C bond [8].

Similarly, when an allyl binds to a C_2 -symmetric catalyst precursor, an analogous picture arises. The C_2 symmetry is broken and, as a consequence of steric interactions, one of the terminal Pd-C bonds is lengthened (Fig. 2). NMR experiments strongly support regioselective alkylation at this position. Thus, not unex-

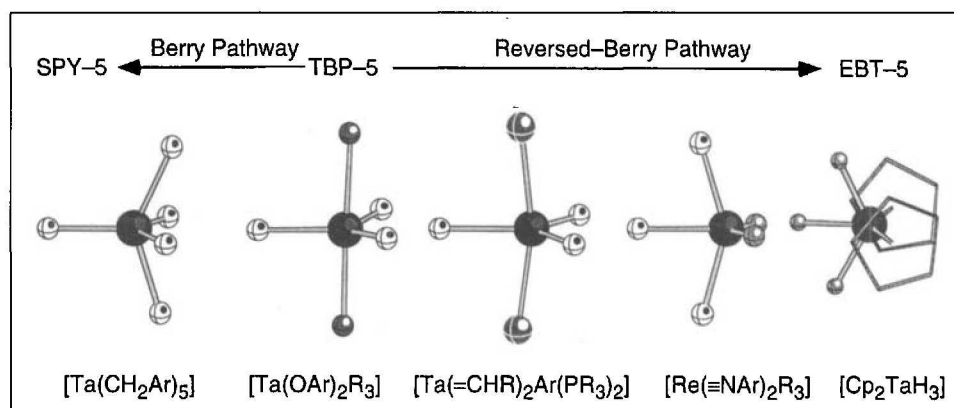


Fig. 1. Mapping of the reverse Berry pathway

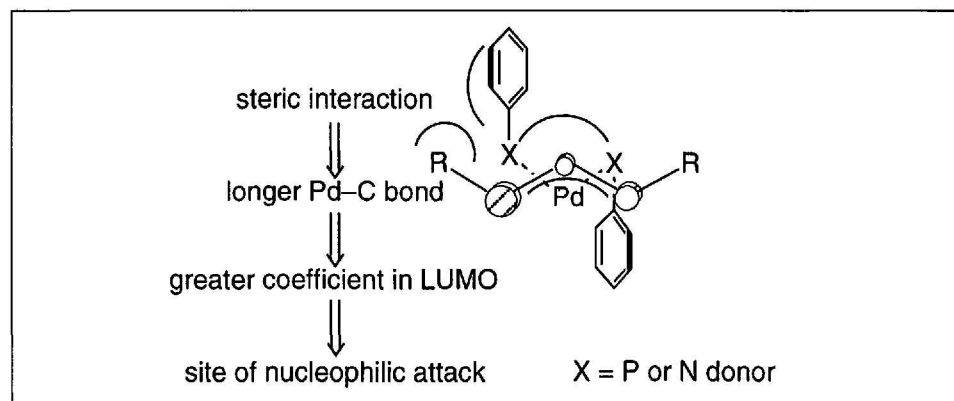


Fig. 2. Frontier-orbital control of the nucleophilic attack on coordinated allyls

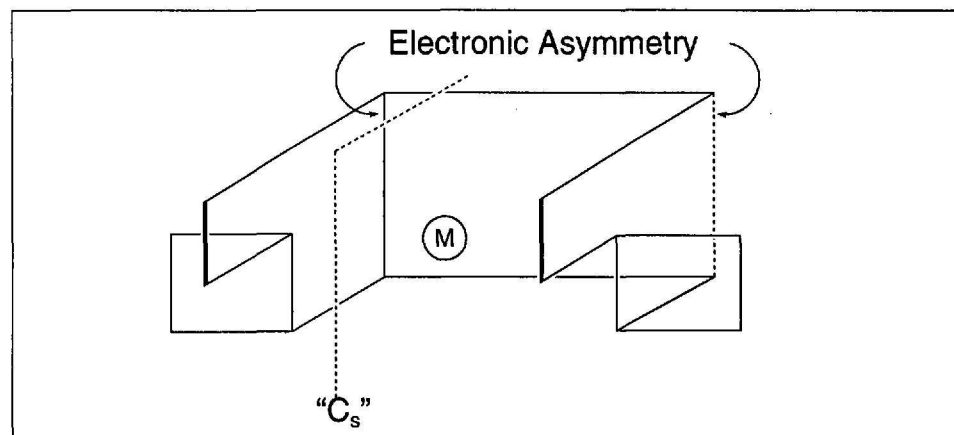


Fig. 3. Pseudo C_s -symmetric ligands displaying electronic asymmetry

pectedly, steric and electronic arguments yield the same result.

We have designed a new class of electronically asymmetric, easily modulable, phosphine-phosphinite bidentate ligands which are pseudo C_s -symmetric (Fig. 3). This guarantees that the enantioselectivity is caused by the electronic asymmetry, as the groove around the metal is nearly achiral from a steric point of view. This should allow us to quantify the importance of electronic asymmetry in various enantioselective catalytic reactions. Preliminary results for allylic alkylations as well as for double bond reduction are highly encouraging and will be published in due time.

3. An Iron-Based Storage Device

Organisms had developed an addiction to iron long before the appearance of dioxygen on earth. Soon thereafter, the primordial soup was rapidly depleted of vital iron, as rust is highly insoluble. Eventually, these organisms released siderophores (iron-sequestering agents) capable of dissolving Fe_2O_3 to capture the precious metal ion. As the Fe^{III} /siderophore complexes are extremely stable, the question arises of how the iron is incorporated into the cell where needed? To date, there are three working hypotheses: 1) Reduction of the Fe^{III} by NADH which yields a labile Fe^{II} /siderophore complex. The iron

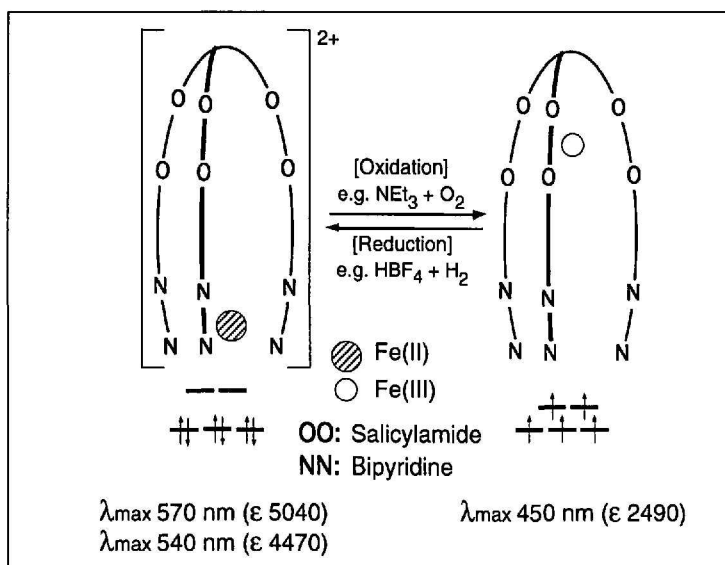


Fig. 4. An iron-based molecular switch

can then be transferred to a softer nitrogen ligand sphere, such as porphyrins, better suited to its oxidation state. 2) Protonation of the Fe^{III}/siderophore, favoring its release. 3) Enzymatic degradation of the siderophore.

In order to mimic the iron release-incorporation mechanism, we [9] and others [10] have designed tripodal ligands

incorporating soft bipyridine and hard salicylamide binding sites. In the presence of a single Fe ion, and depending on its oxidation state, this latter coordinates selectively to one or the other site, displaying very characteristic properties in each case.

Upon oxidation or reduction, the metal ion translocates reversibly, thus allowing

information storage. This molecular device can be addressed by various means, including chiroptical-, Mössbauer-, optical spectroscopy as well as magnetochemical methods (Fig. 4).

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Tailored Receptors for Supramolecular Lanthanide Devices

Claude Piguet*

Although the lanthanide metal ions, Ln^{III}, are considered as the 'chameleons' of coordination chemistry because of their weak dative bonds with common ligands, their variable coordination numbers, and limited stereochemical preferences, their peculiar 4fⁿ electronic configurations have attracted much attention for the design of molecular devices such as contrast agents in MRI, shift reagents in NMR, luminescent stains for fluoroimmunoassays and DNA labelling, and catalysts for selective RNA sequencing [1]. A close structural control of the coordination site and the



Claude Piguet was born in Geneva (Switzerland) in 1961. He studied chemistry at the University of Geneva and received his M.S. degree in Chemistry in 1986. From 1986 to 1989, he was a graduate student at the Department of Inorganic Chemistry of the University of Geneva, where he obtained his Ph.D. thesis with felicitations in 1989 in the domain of coordination chemistry and dioxygen complex-

es. He pursued his formation as a postdoctoral fellow in the group of Prof. J.-M. Lehn at the University of Strasbourg, France (1989–1990), then he returned to Geneva in the group of Prof. A.F. Williams (1990–1994) and finally moved to Lausanne, Switzerland, in the group of Prof. J.-C.G. Bünzli (1995). In 1995, he received the Werner Medal of the New Swiss Chemical Society for his researches in the field of supramolecular chemistry of lanthanide metal ions and luminescent sensors. Since 1995, he is Lecturer in the Department of Inorganic Chemistry at the University of Geneva and recipient of the Alfred Werner Grant for the project 'Toward Organized Luminescent Materials'. His research topics and interests are the methodical studies of self-assembled supramolecular complexes with d-block and f-block metal ions, the development of lanthanide probes and sensors with predetermined structural, photophysical, and magnetic properties, and the preparation of luminescent metallomesogens containing lanthanide metal ions.

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