Electronic Asymmetry: Theoretical Background, Ligand Design, and Applications

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1. Relatives of the d⁶ Bent [Cp₂ML₄] 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 d⁶ organometallic chemistry, the bent metalocene Cp₂M fragment (Cp = cyclopentadienyl) occupies a central position. Considering cyclopentadienyls as six-electron donors occupying a single coordination site, [Cp₂ML₃] complexes may enhance the range of possible applications of free-radical reactions.

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

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Scheme 4

Me₂Al/chiral ligand >90% yield ee 20-34%
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°) (Fig. 1, far right). Let me call this unusual geometry Edge-Bridged Tetrahedral (EBT-5).

The catalytic properties of d⁰ bent metallocenes are remarkable. I need only to mention the stereospecific α-olefin polymerization, where these catalysts are unrivaled 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 [Cp₂ML₃]-like arrangement, the third coordination site occupied by an agostic α-H interaction [6]. This suggested that the catalytic activity of d⁰ bent metallocenes may well be due to the unusual geometry exhibited by [Cp₂ML₃] complexes.

An eHMO study revealed that the EBT-5 geometry is the result of a second-order Jahn-Teller distortion of e' symmetry (in D₃h). In fact, such a distortion from TB-5 corresponds to a reverse Berry pathway. It is favored for all d⁰ systems which contain two properly oriented strong π-donors. This model was tested with a structure-correlation analysis of all five-coordinate d⁰ 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 C₂-symmetric catalyst precursors. Eventually, electronically asymmetric bidentate P,N and P,S ligands were introduced by Palm, 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 C₂-symmetric catalyst precursor, an analogous picture arises. The C₂ 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 unexpectedly, 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 C₂-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 alkylation 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 Fe₂O₃ 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
Tailored Receptors for Supramolecular Lanthanide Devices

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Although the lanthanide metal ions, LnIII, 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 4f 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 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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