

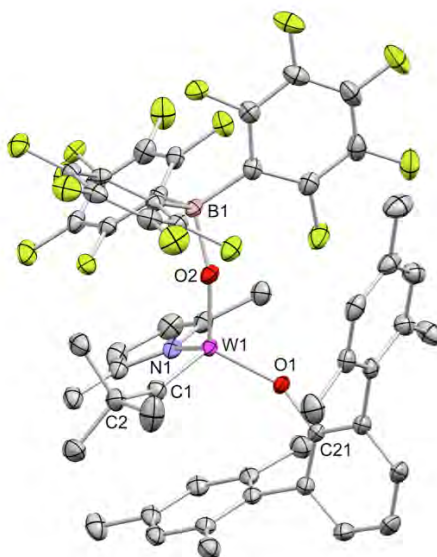
Supplementa to Issue 7-8/2014

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Paracelsus Award Lecture 2014: The Olefin Metathesis Reaction - Approaching Fifty Years of AgeRichard R. Schrock¹¹Massachusetts Institute of Technology

Olefin metathesis, a reaction catalyzed by certain complexes that contain transition metal-carbon double bonds (alkylidene complexes), was discovered in 1956 and therefore is now approaching fifty years of age. The number of sophisticated catalysts and the number of applications in organic and polymer chemistry are still expanding, but in many ways the reaction is still underutilized. This lecture will present a snapshot of some of the recent developments in olefin metathesis with molybdenum and tungsten catalysts, especially tungsten oxo alkylidene complexes. Although "well-defined" tungsten oxo catalysts were discovered approximately 35 years ago, they have been largely unexplored in favor of imido alkylidene complexes of Mo and W. The most important development in the last few years has been the synthesis of MonoAlkoxidePyrrolide (MAP) with the formula $M(X)(CHR')(OR'')(Pyrrolide)$ ($M = Mo$ and $X = NR$; $M = W$ and $X = O$), especially those in which OR'' is a sterically demanding terphenoxide such as 2,6-dimesitylphenoxide (OHMT).



$W(O)[B(C_6F_5)_3](CH-t-Bu)(OHMT)(Me_2Pyr)$.

MAP catalysts offer (*inter alia*) the ability to make *cis* C=C bonds selectively and to behave as initiators for the stereospecific synthesis of polymers through Ring-Opening Metathesis Polymerization (ROMP) of strained cyclic olefins. Polymers with a single tacticity (*isotactic* or *syndiotactic*) can now be prepared, some of which are of commercial interest. Oxo complexes are of special interest since they can be "activated" (reversibly) through binding $B(C_6F_5)_3$ to the oxo ligand (see figure). Other recent applications involving olefin metathesis will be discussed as time allows.

Sandmeyer Award Lecture 2014: Sedaxane, isopyrazam and solatenol: Novel broad-spectrum fungicides inhibiting succinate dehydrogenase (SDH) - synthesis challenges and biological aspects

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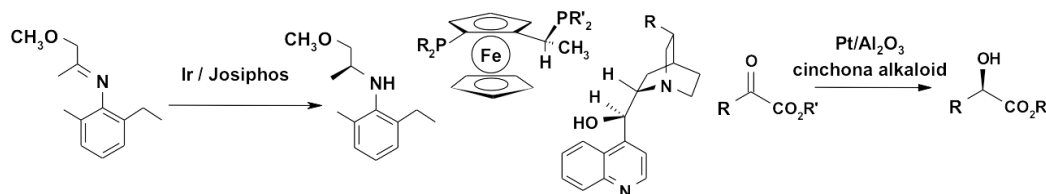
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Sedaxane (SDX), isopyrazam (IZM) and solatenol (STL) are broad-spectrum pyrazole carboxamides which originate from novel classes of agrochemical fungicides. Their mode of action is inhibition of succinate dehydrogenase (SDH), a well known fungicidal mode of action and Carboxin, the first representative of the SDHI carboxamide class was introduced to the market in 1966. A long time the SDHI mode of action was recognized to deliver only compounds with a narrow biological spectrum. This view changed with the market introduction of boscalid in 2003. BASF was the company who first elucidated the potential for broader spectrum of this mode of action. With boscalid, BASF mainly filled their Botrytis portfolio gap, but boscalid also controls other important pathogens such as *Alternaria solani* and *Sclerotinia sclerotium*. Syngenta entered the SDHI area in 1998 and a first goal was the delivery of a foliar cereal compound controlling leaf spots (including *S. tritici*) and rust. With the discovery of the SDHI benzonorbornene amide subclass in 2002, a first breakthrough could be achieved. IZM was derived from this subclass, first prepared in 2003 and entered the market in 2010 (UK). Following up the benzonorbornene area a next breakthrough could be achieved with the synthesis of STL in 2005. STL is a highly efficient fungicide, active against a broad range of pathogens including soybean rust. The high efficacy against soybean rust makes this compound very special and creates huge new business opportunities. STL was introduced to the market in 2012 (Paraguay) and will be introduced to the major soy market Brazil this year. Whereas the 2 Syngenta benzonorbornene compounds have been tailored for foliar use, SDX was specifically designed for seedtreatment use. SDX was first prepared 2002 and entered the market in 2011 (Argentina). All 3 Syngenta SDHIs are very complex from the chemistry synthesis perspective (multistep synthesis and use of new technology). In the lecture the synthesis challenges of SDX, IZM as well as STL will be discussed in detail. New cost-efficient synthesis strategies for the preparation of o-biscyclopropylaniline, new benzonorbornene intermediates and the key pyrazole carboxylic acid intermediate being part of all 3 Syngenta SDHIs, will be in the centre of the discussions.



KGF-SCS Distinguished Industrial Investigator Award Lecture 2014: Looking Back on 35 Years of Industrial CatalysisHans-Ulrich Blaser¹¹St. Gallen (formerly Ciba-Geigy, Novartis and Solvias)

Traditionally, fine and specialty chemicals have been produced using predominantly non-catalytic organic synthesis. This was also true for Ciba-Geigy when I joined their Central Research Laboratories in 1976, even though first efforts were ongoing to study homogeneous catalytic C-C forming reactions. In addition, Ciba-Geigy already had a good tradition in heterogeneous hydrogenation. My colleagues and I were very lucky that over the next 20 years Ciba-Geigy's management strongly supported our ever growing catalysis section for exploring catalytic methods with industrial potential¹⁾. Very early on we decided to concentrate our research on transformations and catalyst types where we expected the biggest potential for the needs of a specialty chemicals company. Due to their versatility for the construction of important structural motifs and for the transformation of functional groups we focused *chemoselective hydrogenation* using modified heterogeneous catalysts²⁾; homogeneous³⁾ and heterogeneous⁴⁾ *enantioselective hydrogenation*, and *homogeneous coupling reactions*⁵⁾. In my lecture, two case studies will be discussed in some detail in order to illustrate our approach to developing catalytic methodology: The enantioselective hydrogenation of C=N bonds with homogeneous Ir-diphosphine complexes allowing the chiral switch of the herbicide Metolachlor²⁾ and the investigation of cinchona modified Platinum catalysts for the asymmetric hydrogenation of activated ketones³⁾. In both cases, we not only solved a specific Ciba-Geigy problem, but also developed generally useful methodologies and could contribute to the understanding of these complex catalytic transformations.



Even more than in academia, success in industrial research relies very heavily on a team effort and the contributions of experts with different know how and expertise. In all my years at Ciba-Geigy, Novartis and Solvias I was very lucky that I could rely on excellent collaborators (for important contributors see the selected references). Without their efforts and dedication none of the results obtained in my 35 years of industrial research would have been possible and I am very grateful to all of them.

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