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Tribute

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Professor Lanny S. Liebeskind

A Tribute

This special issue of Arkivoc is dedicated to Professor Lanny S. Liebeskind on the occasion of his 70th birthday, to acknowledge his important contributions to synthetic organic and organometallic chemistry

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Lanny S. Liebeskind was born in Buffalo, NY in 1950 and studied chemistry at the State University of New York (SUNY) in Buffalo, where he received a B.S. in 1972. He received a Ph. D. in 1976 from the University of Rochester, working with Andrew S. Kende, where he was introduced to the pleasures of total synthesis, in a project where he synthesized Steganicin.[1] He then spent a postdoctoral year at the Massachusetts Institute of Technology, and a second one at Stanford, working with Nobel Laureate Professor Barry Sharpless, where he developed his passion for organometallic chemistry and its applications to organic synthesis. With Prof. Sharpless, Lanny published work on amination reactions using metalloxaziridines.[2]

Prof. Liebeskind started his academic career as Assistant Professor at Florida State University, and moved to Emory University in 1985, where he rose to the rank of Full Professor in 1988, receiving a Samuel Candler Dobbs Chair in Chemistry, a position he still holds. In addition to his research work, which we will later describe, Lanny has served as Chair of the Chemistry Department (1996-2000), as Senior Associate Dean for Research of Emory College (2000-2005), as Director of the Office of University Science Strategies from 2005-2015, and since 2015 as Vice Provost for Strategic Research Initiatives. In 2019 he was asked to oversee the Graduate Division of Biological and Biomedical Sciences at Emory University as its Interim Director. He was a member of the Advisory Board of the Petroleum Research Fund of the American Chemical Society, served from 1990-2014 as an Associate Editor of the journal "*Organometallics*" (ACS), and was an Associate Editor of the "*Encyclopedia of Reagents for Organic Synthesis*" (Wiley) as well as the Editor of "*Advances in Metal–Organic Chemistry*" (JAI Press). He was a Visiting Professor at the University of Iowa, at the Royal Institute of Technology in Stockholm, Uppsala University and the University of Umeå; he also received an Alexander von Humbolt Senior Scientist Research Award, which brought him to the University of Münster.

Among Professor Liebeskind's many awards, I would like to cite an Alfred P. Sloan Foundation Fellowship, a Camille and Henry Dreyfus Foundation Teacher–Scholar Award, a Clifford C. Furnas Memorial Award from S.U.N.Y. Buffalo, a Herty Award from the Georgia Section of the American Chemical Society and a Cope Scholar Award from the American Chemical Society. He was a successful mentor guiding 45 postdoctoral associates, 48 PhD students, 25 Master's degree students, 14 undergraduates and 14 visiting scholars over the course of his career.

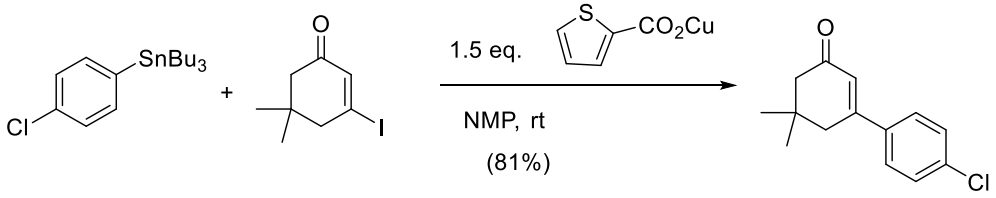
Lanny was for many years a valued consultant to the pharmaceutical industry, and has had long-term commitments to the Bristol-Myers Squibb Company, Pfizer (Monsanto) and Johnson and Johnson. My association with Lanny spans my entire career. Indeed he was one of the first consultants I had contact with in my early days at Bristol-Myers. I found Lanny to be extremely insightful and useful. In those days when Scifinder did not yet exist, Prof. Liebeskind's personal database of papers and reactions was always a valuable source of instant help. As a young scientist, I was sometimes intimidated by some of the older, famous professors coming to visit my company, but I found it easy to work with Lanny, because he was very approachable and about the same age as I was. It was the beginning of a fruitful, ongoing exchange of ideas that enriched my BMS days.

Lanny's research has touched many areas of organic synthesis and organometallic chemistry. I would like to highlight just a few, given the limited space at my disposal.

Copper chemistry for C-C bond formation

At some point during my work at BMS, I became interested in the Stille reaction because of its applications to cephalosporin chemistry, my field of research at the time. Lanny was also interested in it, due to its application to cyclobutenediones, a structural moiety with important applications in synthesis and in medicinal chemistry. In our early exchanges, I informed him on the utility of some ligands for Pd that I had discovered, and he

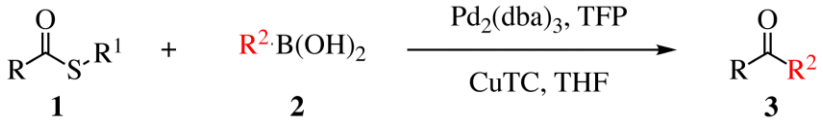
related to me what turned out to be a very important observation: Cu(I) salts were co-catalytic with Pd in some Stille couplings.[3] With his permission, I started delving into it, and confirmed the effect on other substrates; the effect seemed to be general. In our first discussions, I offered a simple explanation for the effect: Cu(I) competes with a Pd(II) species (the resting state of the Stille coupling), and facilitates departure of the ligand from Pd and creates a coordinative unsaturation filled by the reacting stannane. Basically, Cu(I) was helping to create a needed vacancy at Pd(II); however, this could also be done by using ligands of lower donicity and no Cu(I). It was, by my first assessment, a fairly trivial effect. With the support of my management at BMS, Lanny and I started a collaboration to find out what the nature of the Cu(I) effect was, culminating in a full paper which, I am happy to notice, was heavily cited in the years to come (454 times as of this writing).[4] The study confirmed my assumption, but hinted at a "*second copper effect*" in highly dipolar solvents: a transmetalation from Sn to Cu was evidently taking place and was on the reaction path. Although we did not produce any spectroscopic evidence for this intermediate organocopper species (perhaps because the i*n situ* concentration was too low), its kinetic relevance was made clear by selectivity differences in organic group transfer from stannanes *vs*. experiments where no Cu(I) was used. This effect has indeed generated a lot of interest as an early example of "*bimetallic catalysis*": in recent years we have seen this example complemented by a "CuI + fluoride effect",[5] and by bimetallic catalysis using Au,[6] extensions which are both of mechanistic and synthetic interest. Both transmetalation and ligand capture effects have found broad confirmation.[7] In our discussions, Lanny and I agreed that, if transmetalation from Sn to Cu was taking place, then perhaps, under some ideal conditions, we would not need Pd at all! In spite of the generality of Pd couplings in synthesis, the cost of this metal is currently 70 times higher than that of Cu, and its environmental footprint (Kg CO_2 generated to produce 1 Kg of the metal) is >1,000 times higher than that of Cu (which is only twice as high as that of Fe, the most abundant element on earth). In other words, Pd catalysis is becoming unsustainable, and therefore broadening the scope of Cu chemistry was, and still is, a very important area. Lanny then went on to independently show that the Stille reaction can indeed be run without Pd, but usually requires stoichiometric copper. In his first paper of the series, Lanny launched copper(I) thienyl-2-carboxylate (CuTC) as a new regent.[8] An example of this methodology, applied to the coupling of unsaturated stannanes with unsaturated halides, is shown in Scheme 1.



Scheme 1. First example of "Cu-only" Stille-type of coupling.

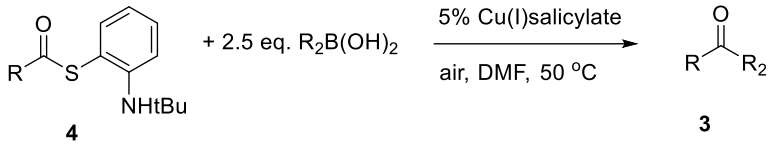
Lanny was also aware that Sn chemistry had limited applicability in industry, given the low Atom Economy of the Stille coupling and the difficulty in removing tin residues from the organic products, and partially reoriented his research toward boron nucleophiles. He soon discovered that Cu(I) is co-catalytic in the Suzuki coupling as well,[9]and that Cu(I) extends the scope of the Stille reaction to substrates like thioethers[10] and thiol esters,[11,12] while thiol esters can also be coupled with organoboron compounds using Pd/Cu catalysis.[13]

The thiol ester-boronic acid coupling, currently called *the Liebeskind-Srogl reaction*, is a new approach to ketones, and in its first embodiment employs Pd/Cu catalysis (Scheme 2).



Scheme 2. First-generation Liebeskind-Srogl ketone synthesis.

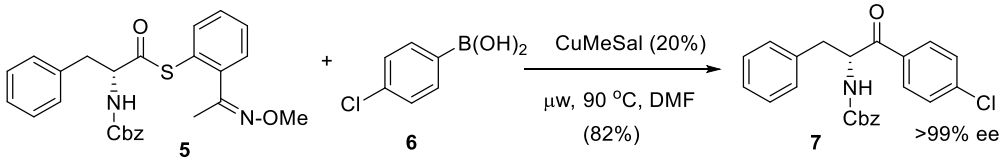
In Scheme 2, R is aliphatic or aromatic, the leaving group (SR^1) can by an alkyl or aryl thiol and the nucleophilic component (R^2) is an unsaturated moiety. TFP is tri(2-furyl)phosphine, a Pd ligand. This approach is also applicable to enantiopure α-amino acid derivatives, which couple without racemization.[14] In an effort to remove the Pd from the cycle and make the reaction catalytic in Cu(I), Prof. Liebeskind successfully developed a second-generation approach, which worked under aerobic conditions and involved a completely new mechanism (Scheme 3).[15] The main drawback of the method is the requirement for at least two equivalents of boronate, because one equivalent reacts with the co-product thiolate.



Scheme 3. Second-generation Liebeskind-Srogl ketone synthesis.

Remarkably, this method, unlike traditional Suzuki couplings which require extremely high pH values, operates at neutral pH, and is suitable for readily racemized substrates, *e.g.* α-amino thiol esters.[16,17] Importantly, the method has been extended to a cyanation under cyanide-free conditions, employing benzyl isocyanide as transfer agent,[18] and to thiation, *e.g.* formation of sulfides using N-thioimides as S transfer agents.[19]

Finally, a third-generation approach to ketone synthesis removes the need for excess boronic acid, and uses a biomimetic strategy (hence the elaborate leaving group in starting material **5**) to effect Cu recycle. In spite of the elevated temperatures needed to carry out this coupling (due to the slow release of Cu back into the cycle), the conditions are neutral, and the reaction works even with racemization-prone α-amino acid derivatives. An example of this general methodology is shown in Scheme 4.[20]

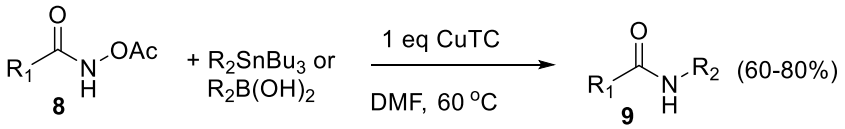


Scheme 4. Third-generation Liebeskind-Srogl ketone synthesis.

Copper chemistry for C-N bond formation

As demonstrated by the fantastic success enjoyed by the Buchwald-Hartwig amination in the pharmaceutical industry and academia alike, catalytic formation of the C-N bond has taken center stage as a field in organometallic chemistry. In addition to developing new approaches to C-C bond formation using Cu catalysis,

Prof. Liebeskind has also made a major impact in this important area. He found that, using a Cu promoter, the N-O bond can be broken and a new C-N bond formed in a number of substrates, *e.g.* hydroxamic acid derivatives like **8** (Scheme 5), thus leading to a new approach to secondary amides.[21] Although the reaction is not catalytic, it employs an inexpensive Cu salt as promoter.



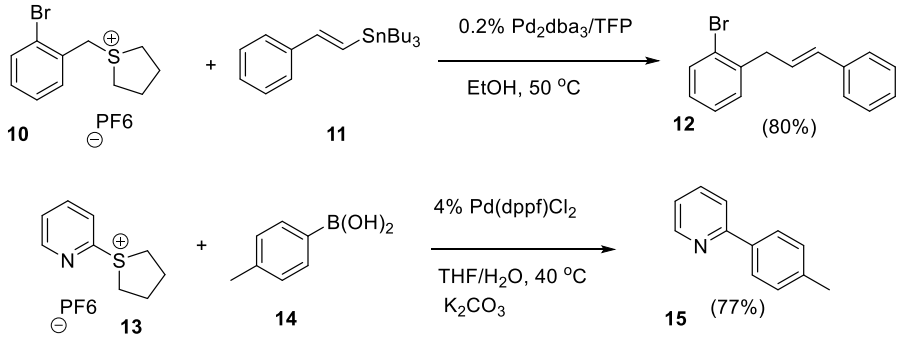
R_1 = alkyl, aryl, heteroaryl; R_2= alkenyl, aryl, heteroaryl

Scheme 5. New synthesis of secondary amides by C-N bond formation.

This approach could be incorporated into a new synthesis of substituted pyridines.[22] A similar approach to imines from ketoximes, resulting in an overall imination, was found to be catalytic in Cu under aerobic conditions.[23] A similar catalytic arylation of *arylnitroso compounds* using Cu(I) catalysts led to a new synthesis of N-aryl anilines.[24]

C-C Cross-coupling with sulfonium salts

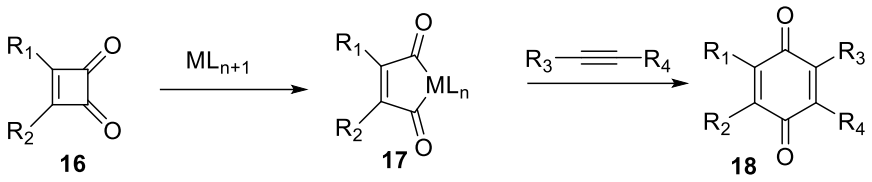
In 1997, Prof. Liebeskind added a new leaving group to the arsenal of cross-coupling electrophiles, *i.e*. the sulfonium group.[25] An impressive number of benzyl, alkenyl, aryl and heteroaryl sulfonium salts were shown to react smoothly with a representative menu of stannanes and boronic acids (Scheme 6). The mild conditions used for these couplings are responsible for the interesting selectivities shown in the scheme (the aryl bromide function in **10** is stable under the reaction conditions). Later, a more effective ligand (triphenylphosphite) was reported for these couplings,[26] and the reaction was extended to acylsulfonium salts, creating a new version of the Liebeskind-Srogl ketone synthesis.[27]



Scheme 6. The coupling of sulfonium salts with stannanes and boronic acids.

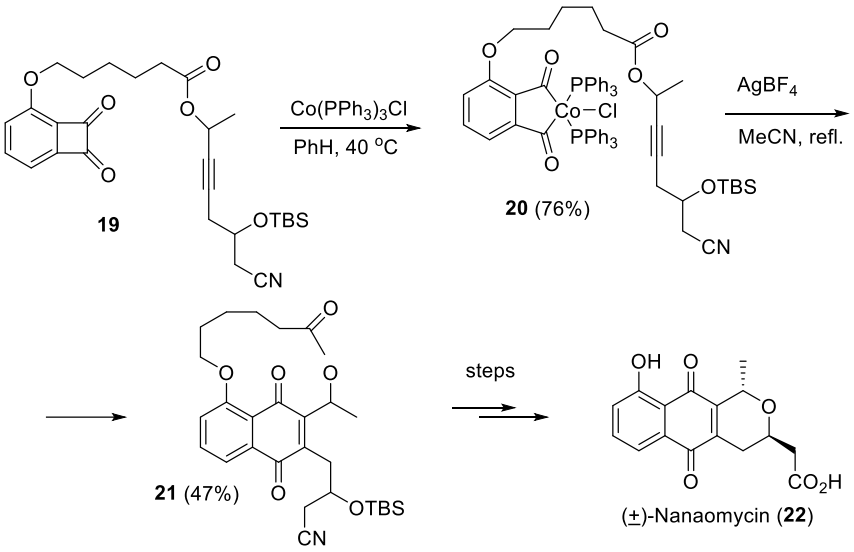
Use of metallacyclopentanones and cyclobutenediones in synthesis

Prof. Liebeskind has pioneered the synthetic use of cyclobutenediones **16** in a variety of synthetically important transformations. Especially fruitful has been the conversion of these building blocks into metallacyclopentenediones **17** (Scheme 7).[28-34]



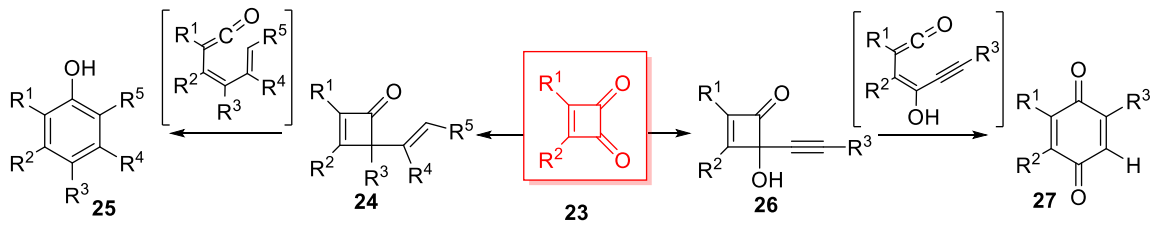
Scheme 7. Use of metallacyclopentenediones in the synthesis of p-quinones (M=Co, Rh, Pd, Ni, Mn).

These species are ideal intermediates for cycloaddition reactions with alkynes, and this is formally equivalent to an insertion of the triple bond into the C-C bond between the two carbonyl groups to yield *p*-quinones (**18**). Many synthetic applications of these methodologies have been reported. An application to the synthesis of quinone antibiotic nanaomycin (**22**) is shown in Scheme 8.[35]



Scheme 8. Total synthesis of racemic Nanaomycin using the new quinone methodology.

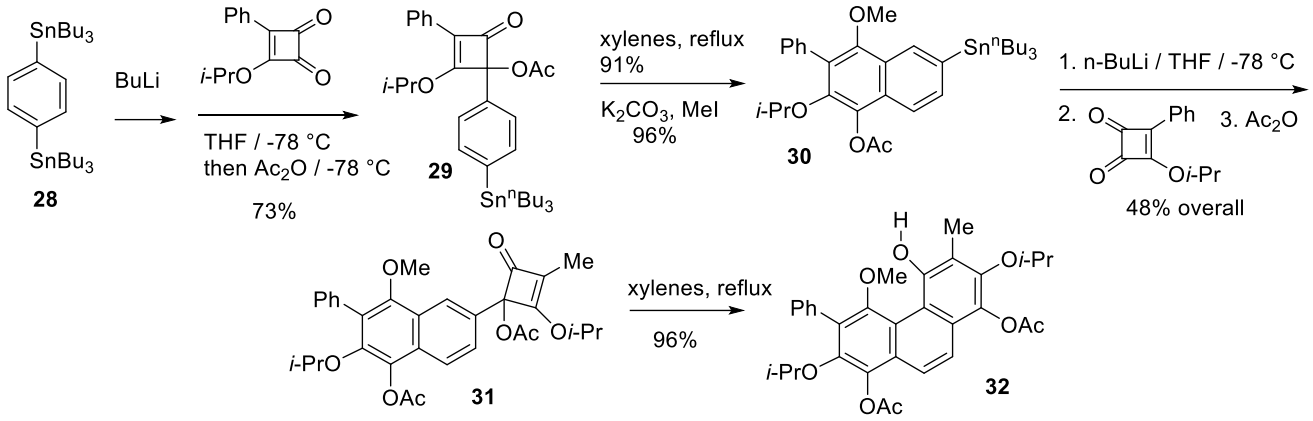
Other transformations of the cyclobutenedione structure involve nucleophilic attack of a vinyl or alkynyl nucleophile at the carbonyl, with subsequent thermolysis to substituted quinones (**27**) or phenols (**25**) (Scheme 9). Thus, substrate **23** reacts at the more reactive of the two carbonyl groups and this is followed by electrocyclic ring opening and re-closure.



Scheme 9. Synthesis of quinones and phenols from cyclobutenediones.

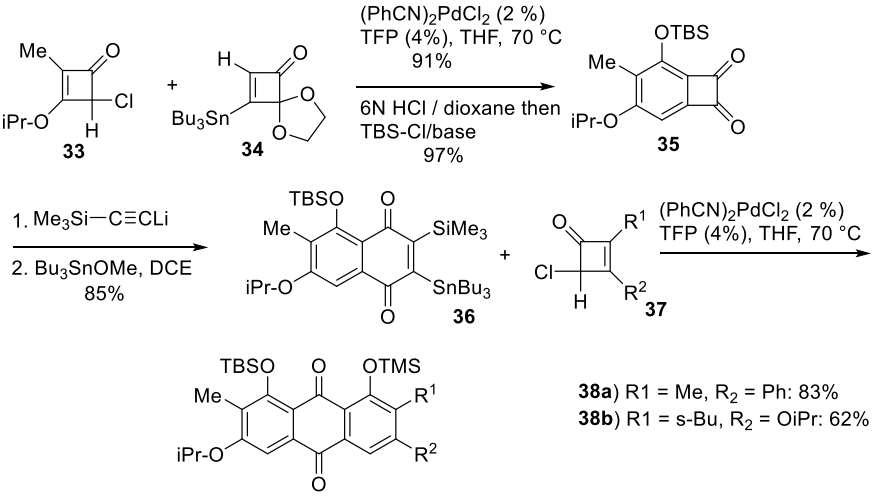
A beautiful extension of this strategy, leading to fused hydroquinone derivatives is shown in Scheme 10. This very elegant example incorporates the above strategy twice, illustrating both a mechanism for complete

site selectivity in the initial attack of the organolithoum species, as well as its potential for sequential applications.[36]



Scheme 10. Example of tandem annulative cyclobutenedione-phenol ring expansion.

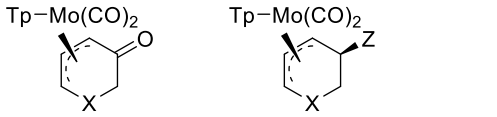
An example of an even more complex strategy, in which three cyclobutenedione building blocks (**22, 34** and **37**) are joined together in sequence to prepare a product featuring three fused aromatic rings (**38a,b**) is shown in Scheme 11.[37]



Scheme 11. Further extension of the annulative strategy based on cyclobutenediones.

Stoichiometric Mo chemistry

Prof. Liebeskind has opened up a fascinating new area of stereoselective synthesis by using optically pure η^3-Mo complexes **39-45** (Figure 1) as substrates to carry out an incredible variety of synthetic transformations, leading to many stereochemically complex natural products containing the piperidine or tetrahydropyran structural motif.[38-60]

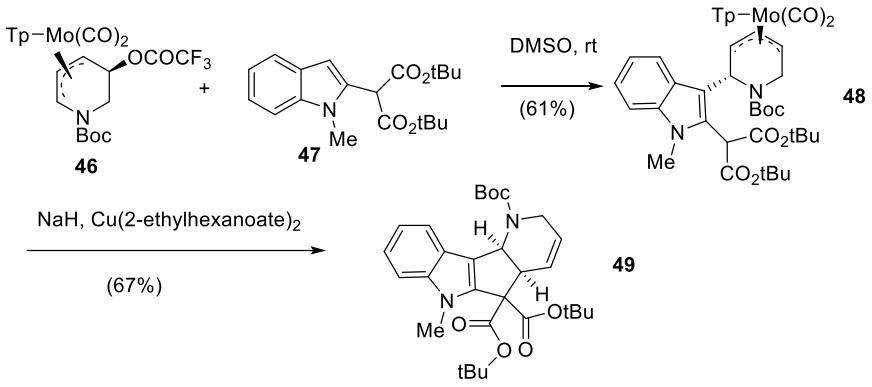


39) X = O,
40) NBoc,
41) NCbz

42) X=O Z=$OCOCF_3$
43) X=O Z=OAc
44) X=NBoc Z=$OCOCF_3$
45) X=NBoc Z=OAc

Figure 1. Allyl molybdenum complexes used in synthesis (Tp=hydridotris(pyrazolyl)borate).

An example of a complex transformation is shown in Scheme 12. Nucleophilic attack at the C-2 position of the ring (terminus of the η^3-allyl complex) is a stereoselective (*anti*) and regioselective operation; this is followed by an intramolecular nucleophilic attack on the resulting Mo complex, forming a second ring under demetallating conditions to yield tetracyclic indole **49**.[61]



Scheme 12. Representative tandem transformation of allyl-Mo complexes.

A complete survey of this methodology is beyond the scope of this brief introduction, but the versatility of this fascinating chemistry is described by Prof. Malinakova's account in this issue.

The future

Prof. Liebeskind, in addition to continuing to develop some of the areas we have just described, has developed a major interest in "Green Chemistry", *i.e*. redeveloping known reactions by introducing new principles that take into account the problematic wastefulness of some of the common methods used today in synthesis. One example is the dehydrative bond-forming reactions used to make esters and amides, including therefore peptides, an important class of drugs. Amidation reactions are usually carried out using complex reagents; to activate the hydroxyl moiety toward acylation and carry out the necessary dehydration process, very large and costly coupling agents are used stoichiometrically, which are a major part of the waste stream at the end of the process. Prof. Liebeskind is now focusing on new catalytic dehydrative methods to mitigate negative environmental and economic impact. A particularly attractive dehydrative bond formation involves the removal of the elements of H_2O through the combined use of an organic oxidant (to accept [2H]) and an organic reductant (to accept [O]). This must be done catalytically to minimize environmental impact. Early results are very encouraging.[62-64]

I wish Prof. Liebeskind continued success in all his research endeavors for many years to come.

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Aachen, Germany

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