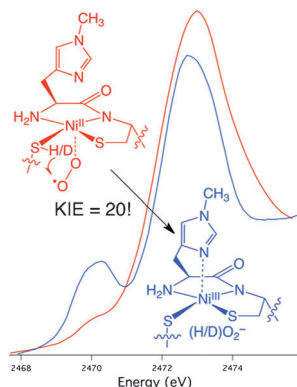


## Enzyme Mechanism

J. Shearer\* 2569–2572



Use of a Metallopeptide-Based Mimic Provides Evidence for a Proton-Coupled Electron-Transfer Mechanism for Superoxide Reduction by Nickel-Containing Superoxide Dismutase



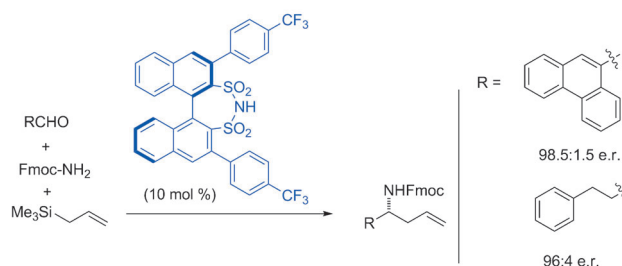
**Sneaky little SOD!** A metallopeptide-based mimic of nickel-containing superoxide dismutase was used to probe the mechanism of superoxide reduction by the metalloenzyme. Kinetic studies suggest a proton-coupled electron-transfer mechanism; large H/D kinetic isotope effects (KIE) are observed. XAS studies suggest the transferred H-atom is in the form of a Ni<sup>II</sup>-S(H)-Cys moiety (see graph).

## Asymmetric Catalysis

S. Gandhi, B. List\* 2573–2576



Catalytic Asymmetric Three-Component Synthesis of Homoallylic Amines



**It takes three to make things go right:** The first direct asymmetric three-component reaction of aldehydes, carbamates, and allyltrimethylsilane leading to enantio-enriched homoallylic amines has been developed using a new chiral disulfon-

imide catalyst (see scheme). The method employs readily available, inexpensive, and nontoxic starting materials and is applicable to both aromatic and aliphatic aldehydes.

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# 50 Years Ago ...

*Angewandte Chemie International Edition* was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

In the first Review of this issue, Günther Wilke described the cyclooligomerization of butadiene using Ziegler-type catalysts, and transition-metal complexes of the resulting products. Wilke was Director of the Max Planck Institute for Coal Research from 1967–1992, and was in fact Ziegler's successor in this post.

The reaction between pentafluorosulfur-chloride and amines was reported in

a Communication by Bernard Cohen and Alan G. MacDiarmid. The resulting adducts were shown to decompose to produce sulfur tetrafluoride, which then reacts further with the amine. MacDiarmid shared the Nobel Prize for Chemistry in 2000 with Hideki Shirakawa and Alan J. Heeger for their work on conductive polymers. A Communication by Heeger on solar cells with a graphene oxide electron-transport layer will be published in Issue 10/2013 to coincide with our 125th Anniversary Symposium.

Reinhard W. Hoffmann reported how the base-catalyzed fragmentation of azobromobenzene derivatives can be used to generate the *o*-bromophenyl anion, which is an intermediate in the formation of benzyne. Hoffmann's account of the changes in natural product synthesis over time was published in our Jubilee Issue 1/2013.

[Read more in Issue 3/1963](#)