Redox-Switchable Catalysis

P. Neumann, H. Dib, A.-M. Caminade,
E. Hey-Hawkins* ______ 311–314

Redox Control of a Dendritic Ferrocenyl-Based Homogeneous Catalyst

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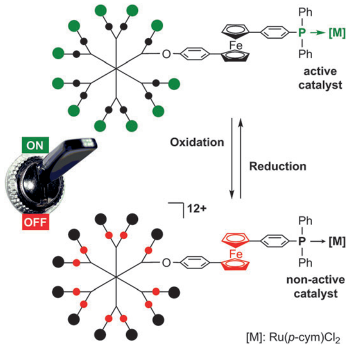
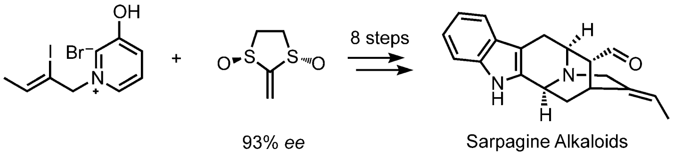


Under control: Both monomeric and dendritic (see picture) ferrocenylphosphane ruthenium(II) catalysts were reversibly switched off and on by chemical oxidation and reduction during isomerization of the allylic alcohol 1-octen-3-ol. This outcome is mainly due to electronic communication between the redox-active unit and the catalytic center. Such redox control could facilitate the development of catalysts with orthogonal activity for different substrates.

Natural Product Synthesis

S. Krüger, T. Gaich* ______ 315–317

Enantioselective, Protecting-Group-Free Total Synthesis of Sarpagine Alkaloids—A Generalized Approach



A general synthesis of sarpagine alkaloids proceeds through an eight-step sequence. The enantioselective total synthesis of (+)-vellosimine, (+)-*N*-methylvellosimine, and (+)-10-methoxyvellosimine has been accomplished without using protecting groups. A “privileged intermediate” is generated in the last step, from which all other members of the alkaloid family can be synthesized.

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Flashback: 50 Years Ago ...

Richard Kuhn et al. reported on the stable triradical 1,3,5-tris-(1,5-diphenylverdazyl-3-yl)benzene, which contains ten conjugated six-membered rings and three unpaired electrons per molecule. Paramagnetic susceptibility and EPR measurements were used to confirm the radical nature of the compound, and it was noted that, unlike related biradicals, its electron spin remained unchanged down to 77 K.

Klaus Hafner et al. discussed the synthesis of pentaleno[2,1,6-def]heptalene. This molecule is a nonbenzenoid isomer of pyrene and can be described as either two pentalene and two heptalene units, or two azulene systems. The compound was of interest for investigating the connection between structure and aromaticity, however it was found that, despite its $4n$ π electrons, the compound was inert toward electrophilic reagents.

The issue also contained several Reviews on, at that time, contemporary topics in organic chemistry. Wolfgang Kirmse summarized the current knowledge of the intermediates of α-elimination reactions, including a discussion of radical and organometallic (carbanion) intermediates; Adolf W. Krebs discussed the properties of cyclopropenium compounds and cyclopropenones, which are Hückel aromatic $(4n+2)$ π-electron systems; and Gert Köbrich detailed the various possible mechanisms of elimination reactions from olefins.

Read more in Issue 1/1965.