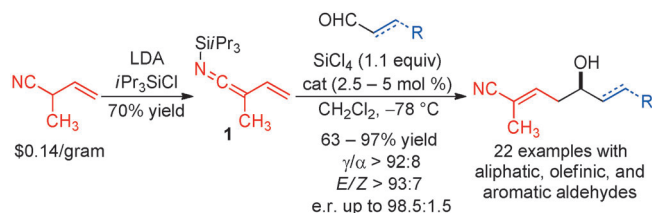


Asymmetric Catalysis

S. E. Denmark,*
T. W. Wilson — 3236–3239



Lewis Base Catalyzed Enantioselective Additions of an *N*-Silyl Vinylketene Imine

Outside the limits: In the title reaction the nucleophile **1** represents a synthetic equivalent of nucleophilic allylic nitriles and addresses some of the current limitations associated with reactions of allylic nitrile anions. Unsaturated nitriles con-

taining a trisubstituted double bond are obtained in high yield, with excellent site selectivity and good to excellent stereoselectivity (see scheme; LDA = lithium diisopropylamide).

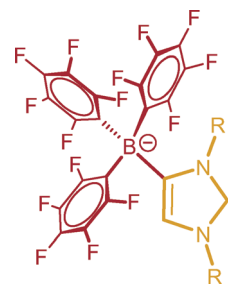
Carbene Chemistry

S. Kronig, E. Theuergarten, C. G. Daniliuc,
P. G. Jones, M. Tamm* — 3240–3244



Anionic N-Heterocyclic Carbenes That Contain a Weakly Coordinating Borate Moiety

Piggyback ride: Anionic N-heterocyclic carbenes are presented that bear their negative charge in the form of a weakly coordinating anionic borate moiety in the backbone. This class of carbene can be used in silver-free routes for the preparation of neutral, single-source gold(I) catalysts, the performance of which is comparable with that of other cationic gold(I) catalysts in enyne rearrangements.



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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.

Already by Issue 4 in 1962, the new *International Edition of Angewandte Chemie* had started to attract contributions from all over the world. In a Communication from the former Czechoslovakia, J. Tomiška and E. Spousta reported the cleavage of the trioxane ring in acetic anhydride solution in the presence of strong mineral acids. The observed reaction was presumed to occur by a cationic cleavage of the ring followed by acylation of the resulting products. Acylated carbodiimides were the subject of two Communications from researchers in Chile, who discussed ring closures and elimination of hydrogen sulfide with these compounds.

Fifty years ago, the measurement of chemical shifts was still relatively new, but the link between the effects mea-

sured by IR and NMR spectroscopy was already being explored. In a Communication, W. Seiffert reported the relationship between the C–H vibrational energy and the chemical shift of the protons in a series of substituted quinolines. A linear relation was found between the chemical shift of an isolated hydrogen atom in a ring and the deformation energy of its out-of-plane vibration.

Side reactions can always be problematic, not least for H. Elsner and S. Saure, who reported an explosion during the uncatalyzed addition of trichlorobromomethane to ethylene in a high-pressure autoclave. Following three incident-free experiments, the autoclave exploded with great force, resulting in the autoclave and manometer being shattered

and the laboratory walls to be covered in soot. It was assumed that a previously unknown side reaction had occurred.

Enzymes were a common theme in the Reviews section, which contained articles on isozymes and heteroenzymes by Theodor Wieland and Gerhard Pfeleiderer, and on microbial enzymes by Christoph Tamm. The latter Review discusses microbial transformations in natural products, including steroids, estrogens, and terpenes. These reactions were valuable in elucidating the biosynthesis and metabolism of the natural products.

[Read more in Issue 4/1962](#)