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RESEARCH FRONT: Photochemistry

Review

Chirality Control in Photochemical Reactions: Enantioselective Formation of Complex Photoproducts in Solution

Christiane Müller, Thorsten Bach

Aust. J. Chem. **2008**, *61*, 557–564.

How can chiral molecules be photochemically created in an enantioselective fashion? With light as a catalyst, chirality information needs to be transmitted from an additional reagent or catalyst to the substrate. Highly productive enantioselective photochemical transformations have been opened up in recent years turning this part of photochemistry into one of the most challenging areas of synthetic organic chemistry.

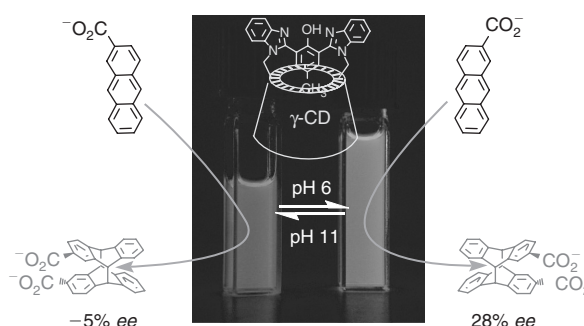
Rapid Communications

pH-Controlled Supramolecular Enantiodifferentiating Photocyclodimerization of 2-Anthracenecarboxylate with Capped γ -Cyclodextrins

Cheng Yang, Chenfeng Ke,
Fujita Kahee, De-Qi Yuan,
Tadashi Mori, Yoshihisa Inoue

Aust. J. Chem. **2008**, *61*, 565–568.

Supramolecular enantiodifferentiating [4 + 4] photocyclodimerization of 2-anthracenecarboxylate mediated by *p*-cresolbisbenzimidazole-capped γ -cyclodextrin was manipulated by solution pH to give the *anti*-head-to-head photodimer of opposite absolute configuration in –5% enantiomeric excess (*ee*) at pH 11 but in 28% *ee* at pH 6.



Facile Photochemical Synthesis of 1,1'-Binaphthyls

Pablo Wessig, Gunnar Müller

Aust. J. Chem. **2008**, *61*, 569–572.

The photochemical synthesis of highly functionalized 1,1'-binaphthyls **9** by photodehydro-Diels–Alder reaction (PDDA) of esters **8** is reported as the first example of an atropselective synthesis of biaryls by a PDDA reaction. Despite rather moderate diastereomeric ratios (up to 32:68), this work should be regarded as proof of concept. Furthermore, the formation of undesired phenanthrenes **10** could be suppressed by introduction of a blocking methoxy group in the 2-position of the naphthyl moiety.

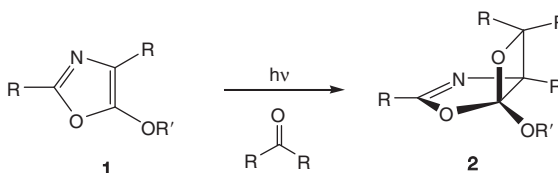
Full Paper

Photocycloaddition of 5-Methoxyoxazoles to Aldehydes and α -Keto Esters: A Comprehensive View on Stereoselectivity, Triplet Biradical Conformations, and Synthetic Applications of Paternò–Büchi Adducts

Axel G. Griesbeck, Samir Bondock

Aust. J. Chem. **2008**, *61*, 573–580.

The photocycloaddition reaction of carbonyl compounds to heteroaromatic substrates is a powerful tool for the synthesis of oxetanes and products derived from oxetanes. The stereoselectivity of the [2 + 2]-photocycloaddition to oxazoles is examined and the results correlated with specific conformations of the intermediate 1,4-biradicals during intersystem crossing. This approach is broadly applicable and serves as a convincing rationale for triplet photocycloaddition stereoselectivities.



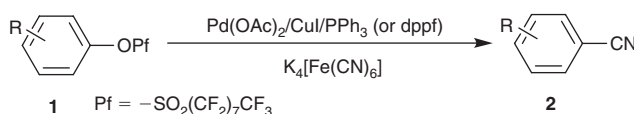
Rapid Communication

Palladium-Catalyzed Cyanation of Aryl Perfluorooctylsulfonates

Yi-Zhong Zhu, Chun Cai

Aust. J. Chem. **2008**, *61*, 581–584.

Cyanation of aryl perfluorooctylsulfonates with potassium hexacyanoferrate(II) catalyzed by an efficient catalyst system comprising $\text{Pd}(\text{OAc})_2$, CuI and PPh_3 or dppf is described. It was shown that the presence of CuI was the key factor in obtaining the corresponding aryl nitriles. Furthermore, the diversity of available phenols and the simple conversion of phenols to aryl perfluorooctylsulfonates and the non-toxic cyanide source make this catalytic reaction attractive as a synthetic method for aryl nitriles.



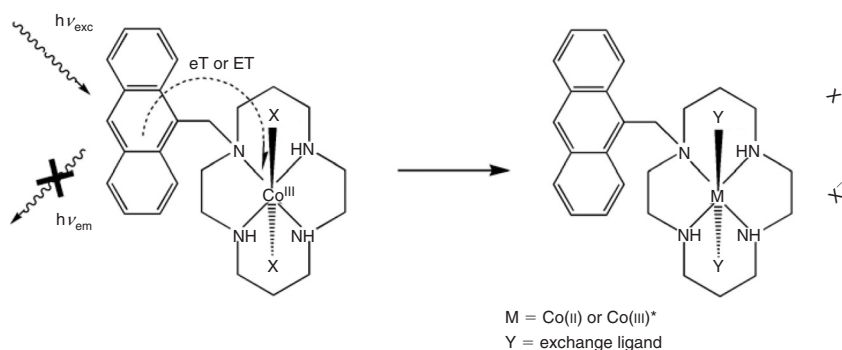
Full Papers

Photochemistry of Anthracene-Appended Cobalt(III) Cyclam Complexes

Simon Boyd, Kenneth P. Ghiggino, W. David McFadyen

Aust. J. Chem. **2008**, *61*, 585–591.

The light-induced release of chemical agents has the potential for use in cancer phototherapy. In this work a photoactivated ligand release process has been demonstrated in an anthracene-appended *cis*-Co(III) cyclam complex. Complexes based on this framework could find future application in targeted drug delivery.



1H-1,3-Diazepines and Ketenimines from Cyanotetrazolopyridines

Chris Addicott, Curt Wentrup

Aust. J. Chem. **2008**, *61*, 592–599.

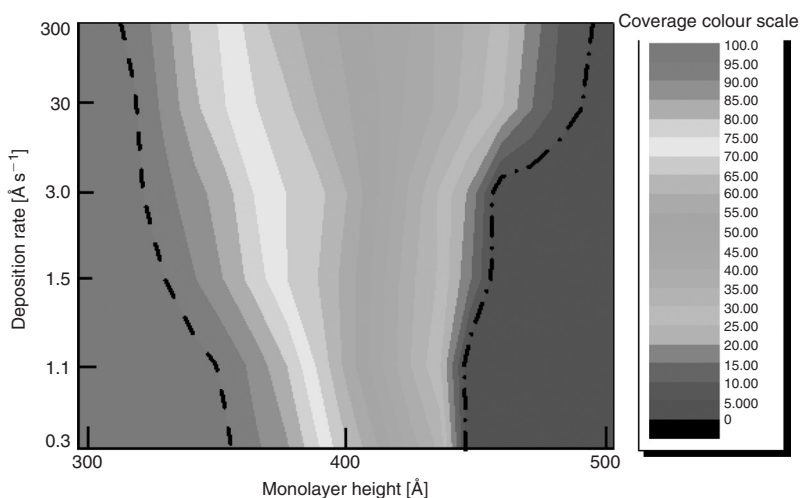
Nitrenes are reactive intermediates of synthetic importance and theoretical interest. It is shown that 2-pyridylnitrenes undergo two competing photochemical reactions, viz. ring expansion and ring opening. This allowed the synthesis of 1,3-diazepines as well as the spectroscopic detection of cyclic carbodiimides and open-chain ketenimines.

Deposition Rate Effect of Alq₃ Thin Film Growth: A Kinetic Monte Carlo Study

Yih-Jiun Lin, Jian-Chuang Chang,
Chin-Kuen Tai, Bo-Cheng Wang,
Feng-Yin Li

Aust. J. Chem. **2008**, *61*, 600–609.

A simple, efficient, and practical simulation method is used to investigate the surface morphology of Alq₃ thin film growth with various deposition rates. The simulation results indicate that there exists a transition growth region in terms of the deposition rate, which corresponds to a transition between the island growth and random deposition growth.

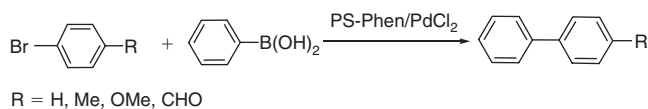


Lewis Acid-Promoted Suzuki Reaction using Palladium Chloride Anchored on a Polymer as a Catalyst

Guozhi Fan, Hanjun Zhang,
Siqing Cheng, Zhandong Ren,
Zhijun Hu, Zilan Wang

Aust. J. Chem. **2008**, *61*, 610–614.

Heterogeneous palladium catalysts have been developed to overcome typical problems in homogeneous catalysis. Palladium chloride anchored on chloromethylated polystyrene modified by 5-amino-1,10-phenanthroline is prepared and used as an efficient recoverable catalyst for the Suzuki cross-coupling reactions. The supported catalyst exhibits high activity for the Suzuki reaction in the presence of Lewis acids.



Solution-Phase Peptide Synthesis; Synthesis of ‘North-Western’ and ‘South-Eastern’ Fragments of the Antifungal Cyclodepsipeptide Petriellin A

Luigi Aurelio, Robert T. C. Brownlee,
Andrew B. Hughes

Aust. J. Chem. **2008**, *61*, 615–629.

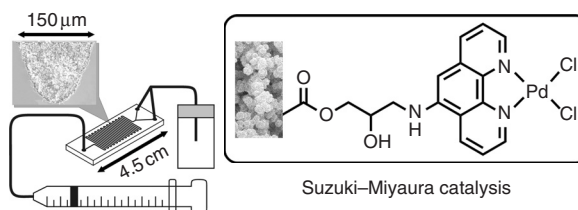
Petriellin A is a modified peptide with antifungal activity, and synthesis of its uncommon peptide bonds is a substantial synthetic challenge. The solution-phase synthesis of two highly modified peptides, a hexamer and a heptamer, that constitute the two halves of Petriellin A is reported. The paper provides new examples of successful syntheses of modified peptides using advanced coupling reagents.

Microfluidic Devices for Flow-Through Supported Palladium Catalysis on Porous Organic Monolith

Allan J. Canty, Jeremy A. Deverell,
Anissa Gömann, Rosanne M. Guijt,
Thomas Rodemann, Jason A. Smith

Aust. J. Chem. **2008**, *61*, 630–633.

Microscale organic synthesis facilitated by palladium catalysis in flow-through mode is feasible in fused silica capillaries and in channels in more robust glass microchips filled with a continuous porous organic polymer monolith. The Suzuki–Miyaura reaction is catalyzed by monolith functionalized with 1,10-phenanthroline groups that has been exposed to palladium(II) solutions. The microreactors are reliable in continuous operation over 96 h with undiminished reactivity and very low leaching of palladium.



Influence of the Crystallization Solvent on the Molecular Structures of Copper(II) Saccharinato Complexes with Pyridazine: Synthesis, X-Ray Crystallography, Spectroscopy, Photoluminescence, and Thermal Properties

Veysel T. Yilmaz, Evrim Senel,
Canan Kazak

Aust. J. Chem. **2008**, *61*, 634–639.

The reaction of $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (sac = saccharinate) with pyridazine (pydz) yield two different complexes, depending on the solvent used in crystallization. $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})(\text{pydz})_2]$ is obtained from the slow evaporation of the reaction solution, while $[\text{Cu}(\mu\text{-OH})(\mu\text{-sac})(\mu\text{-pydz})]_n$ from the diethyl ether diffusion of the same solution. $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})(\text{pydz})_2]$ is paramagnetic, whereas $[\text{Cu}(\mu\text{-OH})(\mu\text{-sac})(\mu\text{-pydz})]_n$ exhibits a significantly low $\mu_{\text{effective}}$ value due to very strong exchange coupling between the copper atoms triply bridged by all three ligands.

Short Communication

Synthesis, Characterization, and Cation-Induced Supramolecular Structures of Photochromic Bisthienylethene-Tetraazaporphyrin Hybrids (BTE-TAPs) Bearing Crown Ether Moieties

Lei Li, Xuan Sun

Aust. J. Chem. **2008**, *61*, 640–645.

Thermally irreversible photochromic diarylethenes that undergo a reversible colour change exclusively with light present significance for potential applications in data storage and molecular switching. The synthesis and photochromism of diarylethene-functionalized tetraazaporphyrin compounds together with their supramolecular structures are reported. This work proposes a novel method to generate multifunctional dyes as well as to extend the research on photochromic diarylethenes from isolated molecules to aggregates for optoelectronic applications.

Focus

Controlling the Fate of Midchain Radicals in Acrylate Polymerization

Thomas Junkers

Aust. J. Chem. **2008**, *61*, 646.

A brief overview is given of the effects that the inherent transfer in polymer reactions leading to the formation of so-called midchain radicals have on acrylate polymerization. Routes to avoid such (mostly unwanted) effects are shown, either via ‘patching’ of the midchain radical defect by use of a dedicated transfer agent or via careful selection of reaction conditions resulting in the formation of uniform unsaturated polymer chains.

