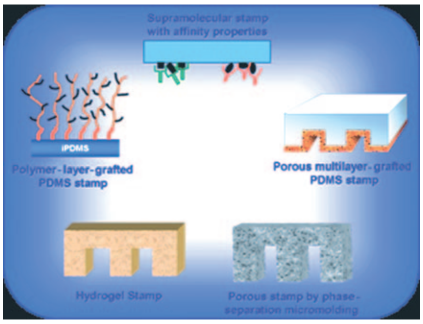
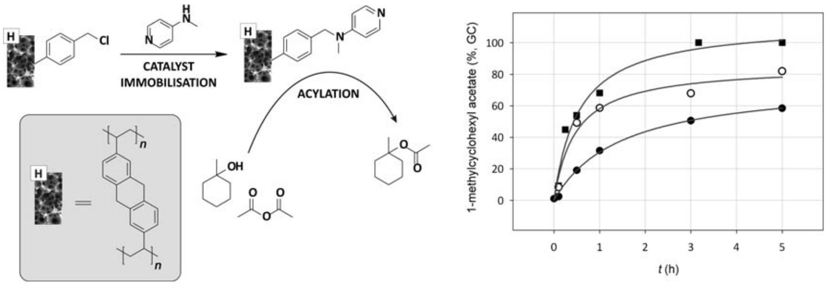
CONCEPTS

Hot off the press! New developments in microcontact printing are focused on the introduction of ink-recognition units in the stamp to selectively bind and transfer inks, and on the use of ink reservoirs integrated within the stamp's design for the repeated transfer of heavy inks, such as biomolecules and nanoparticles (see figure).



Porous Stamps

COMMUNICATIONS

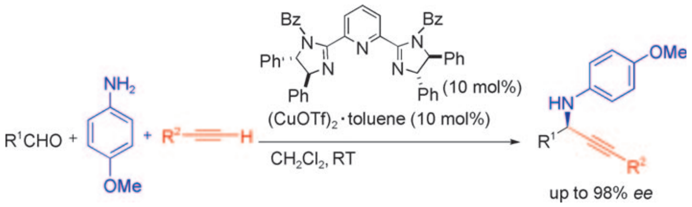


The action is at the surface: Ultra-high surface area emulsion templated porous polymers are prepared by the hypercrosslinking method. Control of the extent of conversion of benzyl chloride groups leaves residual accessible functionality for subsequent immobilisation of 4-(*N*-methylamino)pyridine, giving a highly efficient nucleophilic catalyst that outperforms both un-hypercrosslinked versions and hypercrosslinked polymer beads.

PolyHIPE Organocatalysts

Extraordinarily simple, convenient, and efficient: A general and operationally simple one-pot synthesis of unsymmetrical diaryl sulfides by coupling two different bromoarenes and triisopropylsilanethiol (TIPS-SH) is reported. This protocol overcomes the narrow availability of arene thiols and their instability to oxidation. These reactions catalyzed by palladium complexes generated from the alkylbisphosphine CyPF-*t*Bu occur in good to excellent yields with wide scope and high tolerance of functional groups.

Cross-Coupling Reactions



Enantioselective three-component synthesis of propargylamines from aldehydes, amines, and aliphatic alkynes was catalyzed by a Cu^I complex of 1,3-bis(imidazolin-2-ly)pyridine (pybim). The reaction is applied to a wide variety of aromatic aldehydes and alkynes to give products with excellent yields (up to 93 %) and enantiomeric excess (up to 98 % *ee*) (see scheme; Bz = benzoyl, OTf = trifluoromethanesulfonate).

Asymmetric Catalysis

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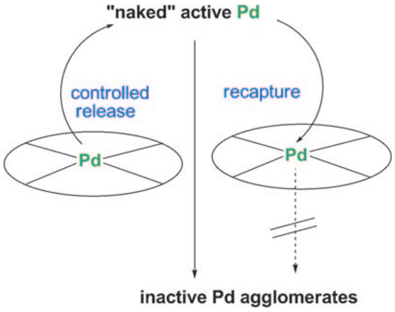
Heck Reaction

*C. Röhlich, K. Köhler** ..... 2363 – 2365

VIP **Tetraalkylammonium-Free Heck Olefination of Deactivated Chloroarenes by Using a Macrocyclic Catalyst Precursor**

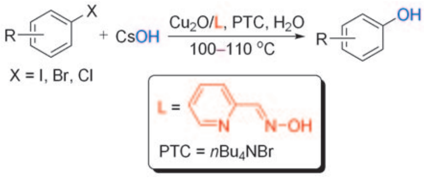


Palladium reservoir: A macrocyclic dinuclear Pd complex is applied to the Heck coupling of strongly deactivated aryl chlorides. The complex serves as a very stable precatalyst, which releases active Pd under normal reaction conditions (see scheme). The controlled release and recapture of active Pd provides sufficient stabilization to supersede the addition of tetrabutylammonium bromide. Quantitative conversions can be achieved under additive-free conditions.

Water Chemistry

*D. Yang, H. Fu** .... 2366 – 2370

A Simple and Practical Copper-Catalyzed Approach to Substituted Phenols from Aryl Halides by Using Water as the Solvent

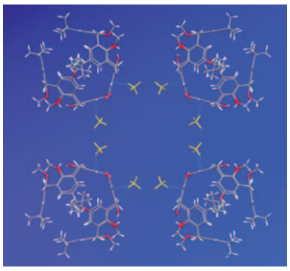


Water surprise! A simple and practical copper-catalyzed approach to substituted phenols by hydroxylation of aryl halides has been developed by using environmentally benign water as the solvent (see scheme). The method proceeds under mild conditions and is tolerant towards various functional groups in the substrates.

Calixarenes

C. Tedesco, L. Erra, M. Brunelli, V. Cipolletti, C. Gaeta, A. N. Fitch, J. L. Atwood, P. Neri** ...... 2371 – 2374

Methane Adsorption in a Supramolecular Organic Zeolite

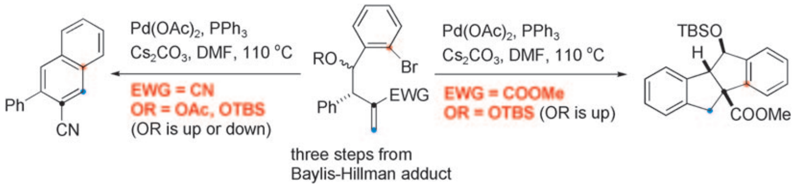


An eight-membered ring: The methane adsorption properties of a new microporous organic zeolite have been studied by volumetric adsorption analysis and high-resolution powder XRD. Methane molecules have been located inside the host channels and a ring of eight methane and eight calixarene molecules is formed through CH π bonds (see figure).

Domino Reactions

*K. H. Kim, H. S. Lee, S. H. Kim, S. H. Kim, J. N. Kim** .... 2375 – 2380

Construction of a Tetracyclic Butterfly-Like Scaffold: Palladium-Catalyzed Heck/Arylation Cascade



Controlled carbopalladation: Only slight changes in the starting material (see scheme) resulted in rather different compounds in palladium-catalyzed domino reactions. A novel tetracyclic butterfly-like scaffold was constructed in a one-pot reaction via the Pd-catalyzed 5-*exo-trig* carbopalladation and arylation cascade in high yield.

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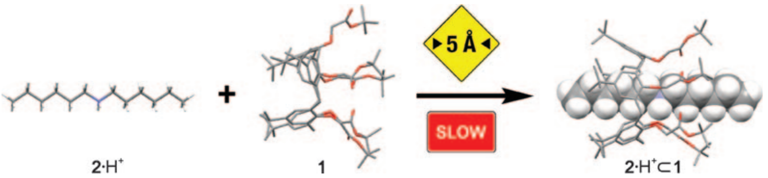
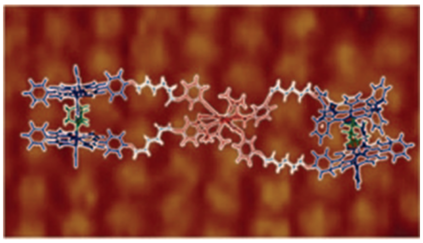
Pseudorotaxanes



Slowly does it! Di-*n*-alkylammonium ions (such as **2**·H$^+$) thread the annulus of calix[5]arene **1** to yield stable [2]pseudorotaxanes. The ease of formation of this hitherto unknown family of interpenetrated supermolecules is predominantly determined by salt ion-pairing effects, whereas the time course of the threading/dethreading process depends on the length of the cation alkylammonium chains.

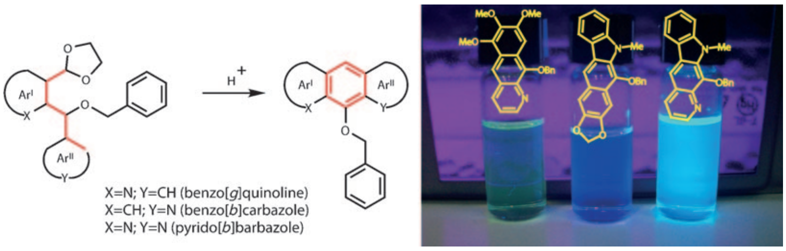
Nanoparticles

Line up! Fourfold zinc porphyrin functionalized perylene bisimide has afforded well-defined supramolecular particles by intramolecular cofacial bridging of zinc porphyrin units through the ditopic ligand DABCO as revealed by UV/Vis and NMR spectroscopy and AFM studies (see figure).



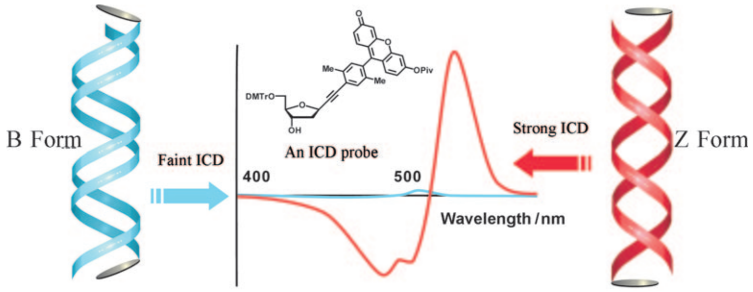
FULL PAPERS

Fused Polycyclic Heteroaromatics



One pot only: A new route to nitrogen-containing, polycyclic, fused aromatics afforded benzo[*g*]quinoline, benzo[*b*]carbazole, and pyrido[*b*]carbazole systems (see figure). These compounds show potential in the field of organic electronics and feature slipped π-stacking interactions in the crystal structure of the benzo[*b*]carbazole system, strong greenish and bluish fluorescence in solution, and large Stokes shifts.

Alkynylnucleosides



Specific ICD for Z-DNAs: An induced circular dichroism (ICD) probe for DNA duplexes was developed on the basis of an alkynyldeoxyribose skeleton (see figure). Strong ICDs were only observed for the Z duplexes of the labeled DNAs.

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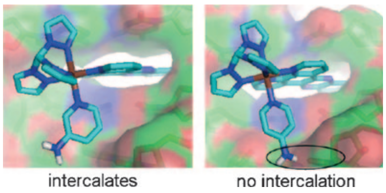
DNA Binding

P. Waywell, V. Gonzalez, M. R. Gill, H. Adams, A. J. H. M. Meijer, M. P. Williamson,* J. A. Thomas** .... 2407 – 2417

Structure of the Complex of [Ru(tpm)(dppz)py]$^{2+}$ with a B-DNA Oligonucleotide—A Single-Substituent Binding Switch for a Metallo-Intercalator



An intercalator switch: The precise nature and positioning of a single substituent on a Ru^{II}(dppz) complex that binds to duplex DNA can tune binding affinities and even switch intercalation on or off (see figure).

Self-Assembly

*T. Weilandt, U. Kiehne, J. Bunzen, G. Schnakenburg, A. Lützen** .... 2418 – 2426

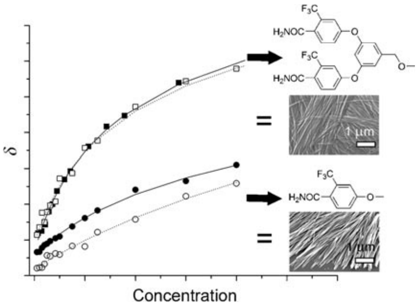
Self-Discriminating Self-Assembly of Dinuclear Heterochiral Rhombs from Tröger's Base Derived Bis(pyridyl) Ligands

Diastereoselective self-assembly: Bis(pyridyl) ligands bearing a 2,8-disubstituted Tröger's base scaffold undergo diastereoselective self-assembly to yield discrete dinuclear achiral metallosupramolecular rhombs upon coordination to *cis*-protected palladium(II) or platinum(II) ions in a self-discriminating manner (see figure), whereas their analogues with a 3,9-disubstituted Tröger's base core do not even assemble selectively in terms of aggregate composition.

Organogelators

*M. Seo, J. H. Kim, J. Kim, N. Park, J. Park, S. Y. Kim** .... 2427 – 2441

Self-Association of Bis-Dendritic Organogelators: The Effect of Dendritic Architecture on Multivalent Cooperative Interactions

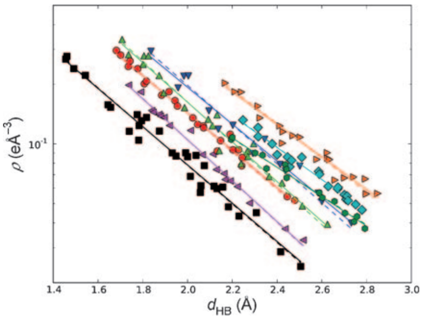


Branching out! A series of bis-dendritic gelators consisting of a benzamide dendron and an alkyl dendron have been synthesized (see figure). Introduction of a dendritic branch was found to promote the formation of a self-assembled fibrillar network by means of multivalent and cooperative hydrogen bonds.

Bond Analysis

*I. Mata, I. Alkorta, E. Molins, E. Espinosa** .... 2442 – 2452

Universal Features of the Electron Density Distribution in Hydrogen-Bonding Regions: A Comprehensive Study Involving H⋯X (X = H, C, N, O, F, S, Cl, π) Interactions



ρ(r) in hydrogen bonds: Topological analyses of the theoretically calculated electron densities for a large set of 163 hydrogen-bonded complexes show that H⋯X interactions can be classified in families according to X (see picture). The observed dependencies between the electron density properties at the bond critical point, as well as between each atom and the bonding distance, are classified as a function of the atomic van der Waals radius or the electronegativity of X.

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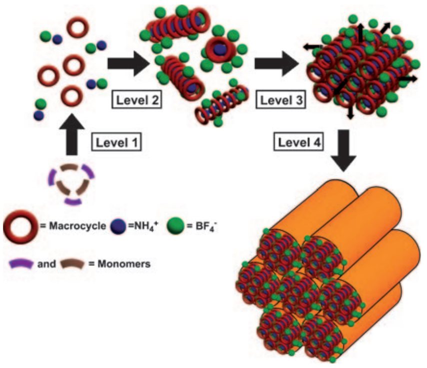
Four-level hierarchical architecture: Schiff base macrocycles, with a diameter of ≈2 nm, undergo ion-induced self-assembly with alkali-metal and ammonium salts to form well-defined, high-fidelity, micron-scale, fibrillar bundles (see figure). This approach may be exploited to develop new materials and synthetic ion channels.



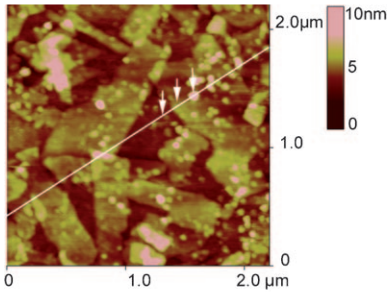
Macrocycles

*J. K.-H. Hui, P. D. Frischmann, C.-H. Tso, C. A. Michal, M. J. MacLachlan** .... 2453 – 2460

Spontaneous Hierarchical Assembly of Crown Ether-like Macrocycles into Nanofibers and Microfibers Induced by Alkali-Metal and Ammonium Salts

---

Film studies: The Langmuir–Blodgett (L–B) technique has been studied and evaluated for the construction of L–B films consisting of surfactant, clay mineral, and lysozyme. The hybrid films were prepared in a controlled way at the water–air interface and were characterized by AFM (see figure) and spectroscopic techniques.



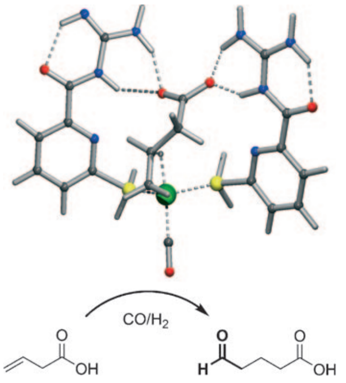
Langmuir–Blodgett Films

*S. D. Miao, H. Leeman, S. De Feyter, R. A. Schoonheydt** .... 2461 – 2469

Three-Component Langmuir–Blodgett Films Consisting of Surfactant, Clay Mineral, and Lysozyme: Construction and Characterization

---

Mimicking enzymes: A library of supramolecular catalysts for hydroformylation of unsaturated acids was prepared. Exploration of the structure–activity relationship and a mechanistic study led to the identification of selective transition-state stabilization by a secondary substrate–ligand interaction as the root of catalyst activity and selectivity (see figure).



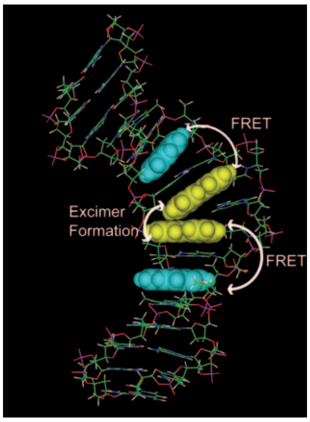
Supramolecular Catalysis

*T. Šmejkal, D. Gribkov, J. Geier, M. Keller, B. Breit** .... 2470 – 2478

Transition-State Stabilization by a Secondary Substrate–Ligand Interaction: A New Design Principle for Highly Efficient Transition-Metal Catalysis

---

Control your excitement! Fluorescence resonance energy transfer between the donor (pyrene) and acceptor (perylene) was observed within the DNA double helix (see figure). In our design, chromophores were arranged in a predetermined order and position. Furthermore, a one-base deletion was successfully detected with a large apparent Stokes' shift.



DNA

*H. Kashida, T. Takatsu, K. Sekiguchi, H. Asanuma** .... 2479 – 2486

An Efficient Fluorescence Resonance Energy Transfer (FRET) between Pyrene and Perylene Assembled in a DNA Duplex and Its Potential for Discriminating Single-Base Changes

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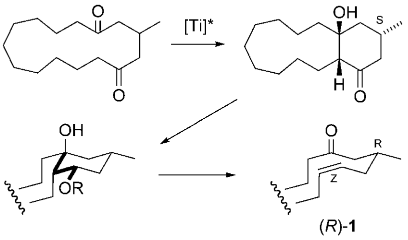
Asymmetric Synthesis

C. Fehr, A. K. Buzas, O. Knopff, J.-Y. de Saint Laumer* .... 2487 – 2495

(+)-(*R*,*Z*)-5-Muscenone and (−)-(*R*)-Muscone by Enantioselective Aldol Reaction and Grob Fragmentation

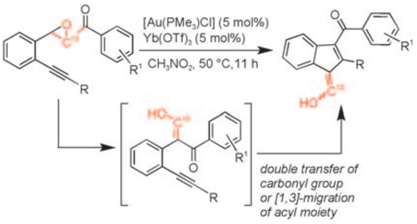


A nose for it: An enantioselective aldol reaction catalyzed by new ephedrine-type Ti reagents was the key step for a new synthesis of the prized fragrance (+)-(*R*,*Z*)-5-muscenone (see scheme).

Gold Catalysis

*L. Z. Dai, M. Shi** .... 2496 – 2502

Gold(I)- and Yb(OTf)$_3$-Cocatalyzed Rearrangements of Epoxy Alkynes: Transfer of a Carbonyl Group in a Five-Membered Carbocycle

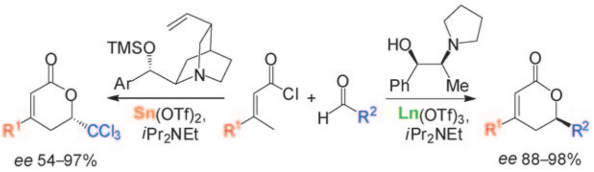


The right mix: A new catalytic system based on a combination of gold(I) and Yb(OTf)$_3$ allows the facile transformation of epoxy alkynes to give novel indene derivatives in moderate to good yields under mild conditions.

Bifunctional Catalysis

*P. S. Tiseni, R. Peters** ...... 2503 – 2517

Catalytic Asymmetric Formation of δ-Lactones from Unsaturated Acyl Halides

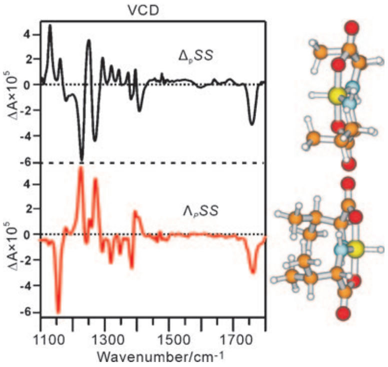


Plus and minus: Zwitterionic dienolates were generated from α,β-unsaturated acid chlorides and utilized as enantiopure diene components in hetero-Diels–Alder reactions to synthesize optically active δ-lactones. Particularly useful are complexes formed in situ from late lanthanide(III) ions, such as Er^{3+} and Yb^{3+}, and a simple commercially available norephedrine-derived ligand (see scheme).

Absolute Configuration

G. Yang, Y. Xu, J. Hou, H. Zhang, Y. Zhao** .... 2518 – 2527

Determination of the Absolute Configuration of Pentacoordinate Chiral Phosphorus Compounds in Solution by Using Vibrational Circular Dichroism Spectroscopy and Density Functional Theory



Combined VCD and DFT: The absolute configurations of four pentacoordinated chiral phosphorus compounds in solution have been determined by using vibrational absorption (VA) and vibrational circular dichroism (VCD) spectroscopy in combination with density functional theory. The sensitivity of the VA and VCD (see figure) spectra to structural isomerism and to stereogenic centers located at the phosphorus atom and chiral ligands has been investigated.

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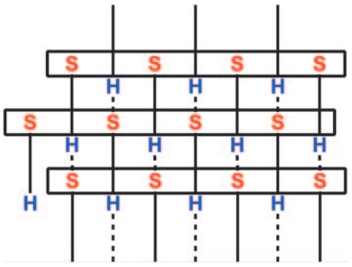
Layer by layer: Guanidinium 1-propynesulfonate crystallizes with a “standard” single-layer structure in which $CH_3C\equiv C$ groups lie alternately above and below the mean plane of each sheet. Guanidinium ethynesulfonate also crystallizes with a single-layer stacking motif, but, unlike the propyne derivative, all the sheets have the $HC\equiv C$ groups pointing in the same direction. $C_{sp}-H\cdots O$ hydrogen bonding between sulfonate anions is responsible for this unusual situation (see graphic).

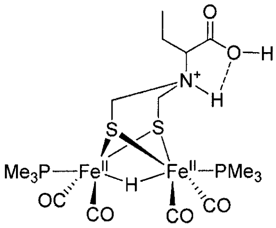


Crystal Engineering

*K. Bouchmella, S. G. Dutremez,**
C. Guérin, J.-C. Longato,
F. Dahan .... 2528 – 2536

Guanidinium Alkynesulfonates with Single-Layer Stacking Motif: Interlayer Hydrogen Bonding Between Sulfonate Anions Changes the Orientation of the Organosulfonate R Group from “Alternate Side” to “Same Side”

Novel hydrogenase mimics: Azapropanedithiolate-bridged model complexes of [FeFe]-hydrogenase bearing a carboxylic acid functionality have been designed, with the aim of decreasing the potential for reduction of protons to hydrogen. This was observed for complex **1**, presumably due to the intramolecular hydrogen bond.



1

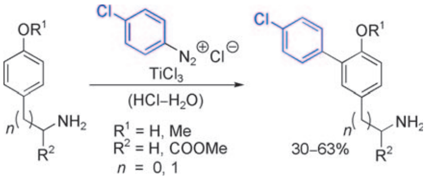
Bioinorganic Chemistry

W. Gao, J. Sun, T. Åkermark, M. Li,
L. Eriksson, L. Sun,
*B. Åkermark** .... 2537 – 2546

Attachment of a Hydrogen-Bonding Carboxylate Side Chain to an [FeFe]-Hydrogenase Model Complex: Influence on the Catalytic Mechanism

---

A revelation in arylation! Radical arylations of *para*-substituted phenols, phenyl ethers, and furans proceed with good regioselectivity at the *ortho* position of hydroxy- or alkoxy-substituted phenyls or at the 2-position of furans. The reactions are conducted with arenediazonium salts as aryl radical sources, titanium(III) chloride as the reductant, and diluted hydrochloric acid as the solvent (see scheme).

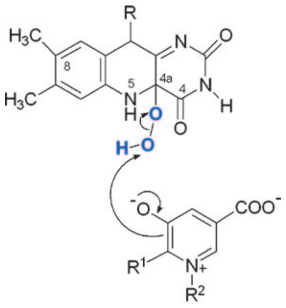


Radical Reactions

A. Wetzel, G. Pratsch, R. Kolb,
*M. R. Heinrich** .... 2547 – 2556

Radical Arylation of Phenols, Phenyl Ethers, and Furans

How to digest a vitamin: The bacterial ring-opening mechanism of vitamin B_6 was explored, and two new pathways are reported herein. The newly proposed mechanisms are in accordance with all experimental information presented to date (see scheme).



Enzyme Reaction Mechanisms

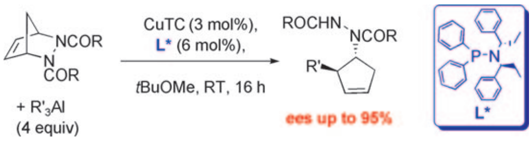
B. Tian, Y. Tu, Å. Strid,
*L. A. Eriksson** .... 2557 – 2566

Hydroxylation and Ring-Opening Mechanism of an Unusual Flavoprotein Monooxygenase, 2-Methyl-3-hydroxypyridine-5-carboxylic Acid Oxygenase: A Theoretical Study

Desymmetrisation Reactions

*L. Palais, C. Bournaud, L. Micouin, A. Alexakis** .... 2567 – 2573

Copper-Catalysed Ring Opening of Polycyclic *meso*-Hydrazines with Trialkylaluminium Reagents and SimplePhos Ligands

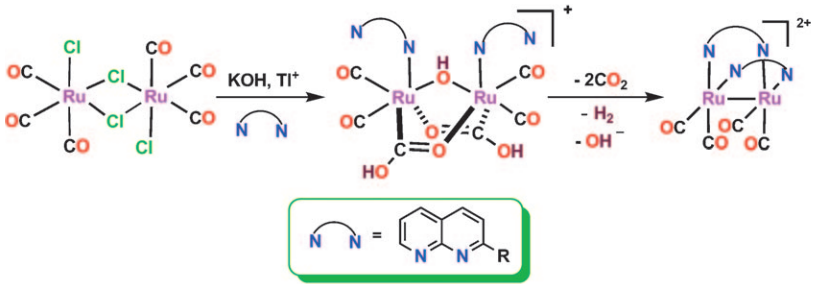


Symmetry isn't everything: *meso*-Hydrazines could be desymmetrised by ring-opening reactions with various metal catalysts to form substituted cyclopentenes (see scheme; CuTC = copper thiophene carboxylate), which have high synthetic potential. Thus, the copper-catalysed asymmetric ring opening of a range of polycyclic hydrazines with trialkylaluminium reagents and SimplePhos ligands (**L***) occurs in excellent isolated yields and high *ee*s.

Bimetallic Chemistry

*M. Majumdar, A. Sinha, T. Ghatak, S. K. Patra, N. Sadhukhan, S. M. W. Rahaman, J. K. Bera** .... 2574 – 2585

Mapping the Transformation $[\{Ru^{II}(CO)_3Cl_2\}_2] \rightarrow [Ru^{I}_2(CO)_4]^{2+}$: Implications in Binuclear Water–Gas Shift Chemistry

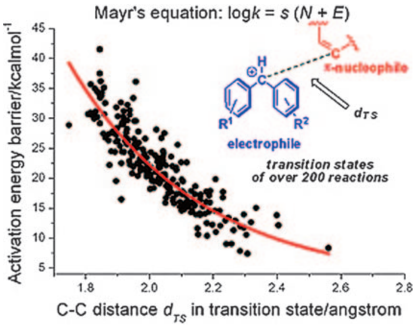


Cartographic chemistry: The base-promoted reaction of $[\{Ru^{II}(CO)_3Cl_2\}_2] \rightarrow [Ru^{I}_2(CO)_4]^{2+}$ proceeds through the intermediacy of a μ-OH, μ:κ^2-*C*,*O*-CO_2H-bridged diruthenium(II) complex, followed by decarboxylation and subsequent dinuclear reductive elimination of molecular hydrogen with the concomitant formation of a Ru^{I}–Ru^{I} bond (see scheme).

Nucleophilicity Scales

C. Wang, Y. Fu, Q.-X. Guo, L. Liu** .... 2586 – 2598

First-Principles Prediction of Nucleophilicity Parameters for π Nucleophiles: Implications for Mechanistic Origin of Mayr's Equation

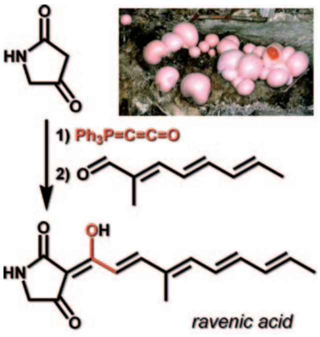


An ab initio protocol was developed to predict the nucleophilicity *N* parameters of various π nucleophiles through transition-state calculations. The success of predicting *N* parameters from first principles also allowed for in-depth analysis of the electrostatic, steric, and solvation energies involved in electrophile–nucleophile reactions. For example, the observed correlations of the electrophile–nucleophile C–C distances in the transition state with the activation energy barriers (see picture) as well as the *E* and *N* parameters indicate the importance of steric interactions in Mayr's equation.

Antibiotics

*A. Schlenk, R. Diestel, F. Sasse, R. Schobert** .... 2599 – 2604

A Selective 3-Acylation of Tetramic Acids and the First Synthesis of Ravenic Acid



Two double bonds from one ylide: Tetramic and tetronic acids react with Ph_3PCCO (see scheme) to give exclusively and quantitatively the corresponding 3-acyl ylides. Once deprotonated with KO*t*Bu they undergo an *E*-selective Wittig reaction with aliphatic and aromatic aldehydes. Even delicate 3-oligoenoyl tetramic acids, such as the natural antibiotic ravenic acid are accessible in good yields. New biological properties are reported.

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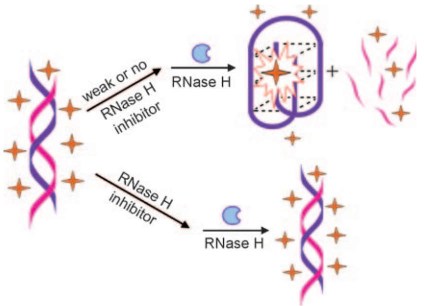
Enzyme Assays

D. Hu, F. Pu, Z. Huang, J. Ren, X. Qu* 2605–2610

A Quadruplex-Based, Label-Free, and Real-Time Fluorescence Assay for RNase H Activity and Inhibition 💻

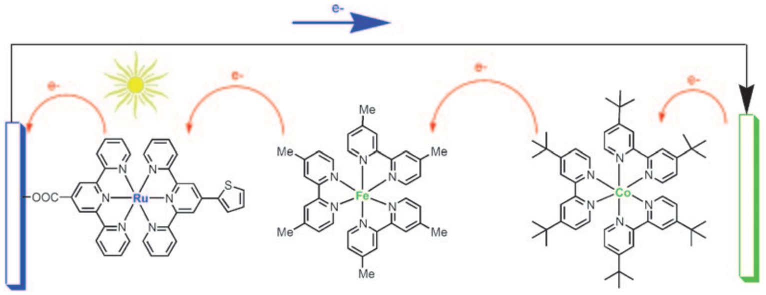


Catching RNase H in the act: A unique quadruplex-based fluorescence assay for sensitive, facile, real-time, and label-free detection of RNase H activity and inhibition has been demonstrated (see figure). The assay takes advantage of the large fluorescence enhancement arising from specific binding of *N*-methyl mesoporphyrin IX by G-quadruplex DNA, and offers an ideal system for high-throughput screening of enzyme inhibitors.

Solar Cells

S. Caramori, J. Husson, M. Beley, C. A. Bignozzi, R. Argazzi, P. C. Gros** 2611–2618

Combination of Cobalt and Iron Polypyridine Complexes for Improving the Charge Separation and Collection in Ru(terpyridine)$_2$-Sensitised Solar Cells 💻

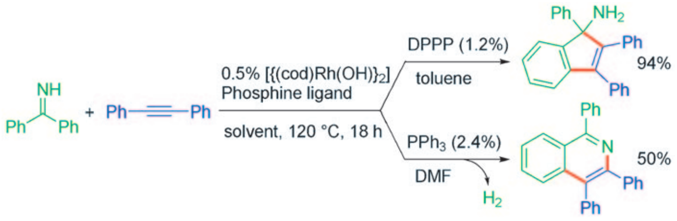


Electron-transport shuttle: The ground state of ruthenium–thienylterpyridine dyes was regenerated very efficiently by a mixture of noncorrosive iron and cobalt complexes as an electron relay (see illustration). The efficiency of the regeneration cascade was critically dependent on the ability of the iron complex to capture cobalt centres, as was clearly demonstrated by chronocoulometry experiments. A promising route for improving the performance and stability of dye-sensitised solar cells (DSCs) has been opened.

Annulation Reactions

*Z.-M. Sun, S.-P. Chen, P. Zhao** 2619–2627

Tertiary Carbinamine Synthesis by Rhodium-Catalyzed [3+2] Annulation of N-Unsubstituted Aromatic Ketimines and Alkynes 💻



Depending on the phosphane ligand and solvent polarity, Rh^I-catalyzed 1:1 coupling of N-unsubstituted aromatic ketimines and internal alkynes led to [3+2] annulations to form indene-based tertiary carbinamine products, or [4+2] annulations to form isoquinoline products (see scheme).

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