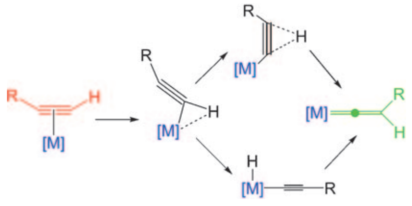
CONTENTS

MINIREVIEWS

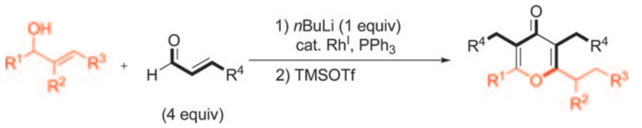
Coordination Chemistry



How to tautomerise alkynes: Transition-metal vinylidene complexes are important synthetic intermediates for a range of transformations involving terminal alkynes. This article reviews a number of recent developments focused on understanding the alkyne/vinylidene tautomerisation mediated by transition-metal complexes. The coupling of experimental and theoretical methods has allowed for detailed insight into this process and the factors which control it.

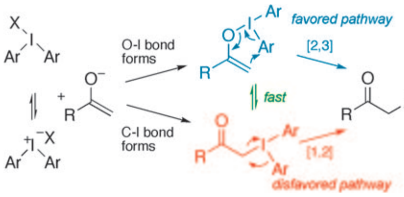
COMMUNICATIONS

Homogeneous Catalysis



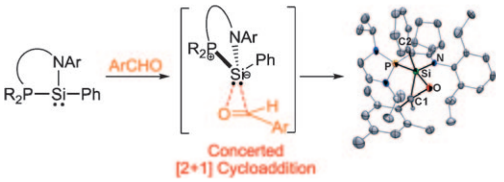
All together now! A unique Rh^I-catalyzed reaction was developed to produce γ-pyrones, which are 1,3,5-triketone equivalents. This reaction was thought to proceed by three redox reactions of allylic alcohols, two intermolecular aldol reactions of α,β-unsaturated aldehydes, and one intramolecular aldol reaction to afford 1,3-cyclohexanediones, which were then converted into γ-pyrones (see scheme; TMSOTf = trimethylsilyl trifluoromethanesulfonate).

Hypervalent Arylation



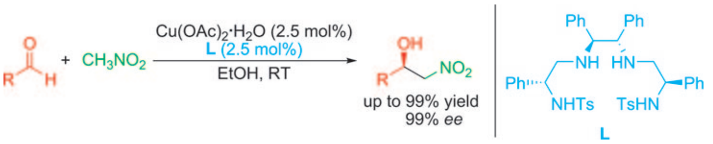
Surprising equilibration: A new mechanism for the title reaction is supported by DFT calculations and experimental observations. The C–I and O–I intermediates are isoenergetic and equilibrate quickly. Thus, any chiral information induced in the initial complex will be destroyed. In the final C–C bond-forming step, a [2,3]-rearrangement from the O–I bonded intermediate is slightly preferred over the [1,2]-elimination from the C–I bonded isomer (see scheme).

Silicon Compounds



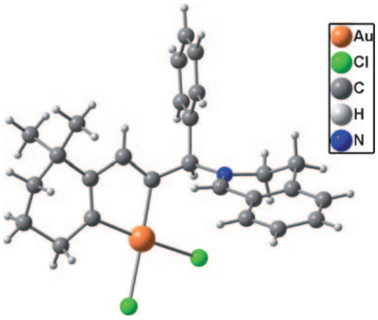
Stabilising the core: Contrary to the case of non-stabilised transient silylenes, which react with carbonyl compounds to form donor–acceptor adducts, the reaction of a phosphine-coordinated silylene with an aldehyde proceeds by a concerted [2+1] cycloaddition with a very low energy barrier to afford a pentacoordinate oxasilirane (see scheme). This result clearly demonstrates the behaviour of phosphonium sila–ylides as nucleophilic silylenoids.

Asymmetric Catalysis



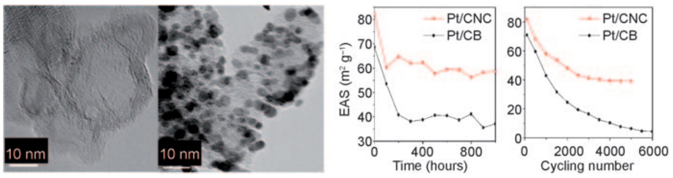
A skeleton in the closet! As a unique chiral skeleton, the newly developed bis(sulfonamide)–diamine, which contains both diamine and bis(sulfonamide) moieties, was a highly effective ligand for the asymmetric $Cu(OAc)_2$-catalyzed Henry reaction between nitromethane and aldehydes with a low catalyst loading at room temperature (see scheme). Both aliphatic and aromatic aldehydes gave excellent enantioselectivities of up to 99 % *ee.*

Reaction Mechanisms



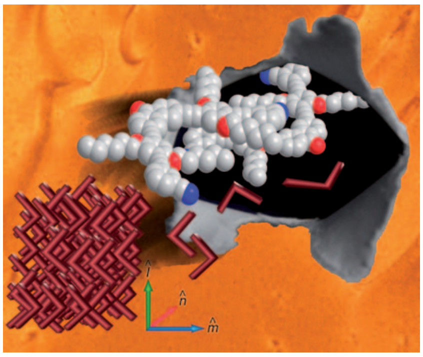
Golden ring: A route for the direct $AuCl_3$-catalyzed conversion of an enyne–amine into cyclopentadiene is reported. The mechanism for the catalysis is proposed and supported by a resting-state zwitterionic gold(III)-cyclopentadiene structure (see figure).

Nanoparticles



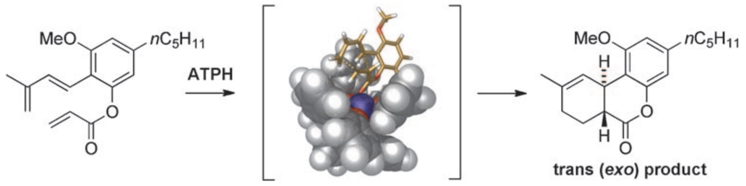
Graphitic carbon is the key: A Pt catalyst that is supported on carbon nanocages with a graphitic structure is found to exhibit not only a high catalytic activity, but also a superior thermal stability and electrochemical durability in harsh operating conditions when compared with a counterpart that is supported on conventional carbon black (see graphic).

Liquid Crystals



Line up! Two optical axes in nematic phases make high demands on the mesogen design. V-shaped, shape-persistent fluorenone nematogens have been shown to assemble in low-temperature nematic liquid-crystal phases with biaxial order (see figure).

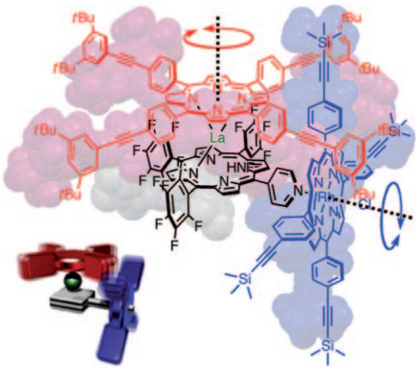
Cycloaddition Reactions



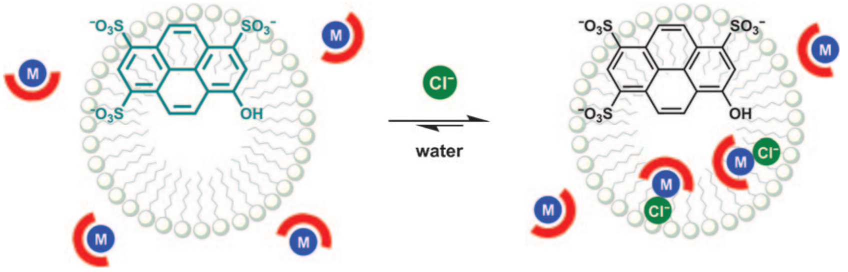
Reversal of fortune: The inherent *cis* stereoselectivity of an intramolecular Diels–Alder reaction is reversed through promotion with aluminum tris(2,6-diphenylphenoxide) (ATPH), allowing a total synthesis of the natural product Δ^9-tetrahydrocannabinol (see scheme). Computational studies predict the experimental findings and shed light on the stereocontrolling influences at play in these Diels–Alder reactions.

Molecular Machinery

Supramolecular rotor: The interlocking of two porphyrin-based molecular rotors into a bevel-gear-shaped structure is demonstrated (see figure). The mechanical interactions between the teeth of the two porphyrin rotors enabled them to mesh and rotate with almost identical activation energies. Switching the rotational activities of one rotor by using chemical stimulation induced a change in the cooperative rotational motions of both rotors.



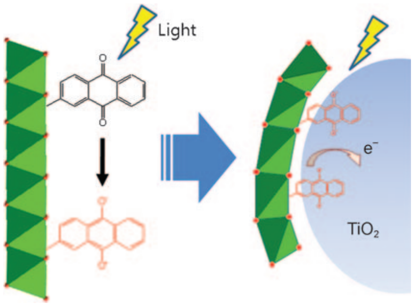
Chemosensors



Caught in a trap! Fluorimetric chloride sensing in water is achieved by exploiting the changes in partition constant of a receptor complex in its bound and unbound states. In the presence of chloride, the complex preferentially resides in the micelle pseudo phase, where its contact with a fluorescent dye results in pronounced quenching effects (see figure).

Photochromism

Hybrid light sensitizer: The exfoliated, layered, double hydroxide nanosheets induced a strong photochromic function in the anthraquinone sulfonate anions that were chemically immobilized on the nanosheets. This hybrid nanosheet was applied to the dye-sensitized solar cell as a new light sensitizer that was self-organized on TiO$_2$ spheres, resulting in a higher solar-to-electric conversion efficiency than the single-dye cell, owing to the intense photochromic function of the hybrid nanosheets.

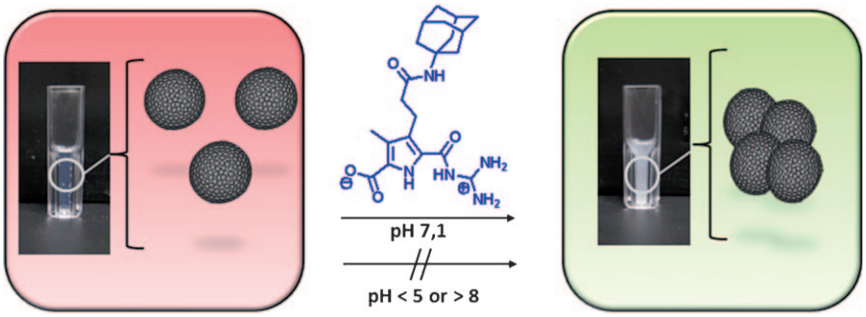


FULL PAPERS

Host–Guest Interactions

J. Voskuhl, T. Fenske, M. C. A. Stuart, B. Wibbeling, C. Schmuck, B. J. Ravoo** .... 8300 – 8306

Molecular Recognition of Vesicles: Host–Guest Interactions Combined with Specific Dimerization of Zwitterions

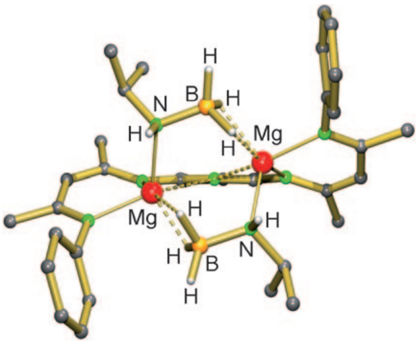


Vesicles in close contact: Cyclodextrin vesicles stick together due to a combination of two supramolecular interactions, that is, host–guest inclusion and dimerization of zwitterions (see figure).

Magnesium Amidoboranes

*J. Spielmann, D. F.-J. Piesik, S. Harder** .... 8307 – 8318

Thermal Decomposition of Mono- and Bimetallic Magnesium Amidoborane Complexes

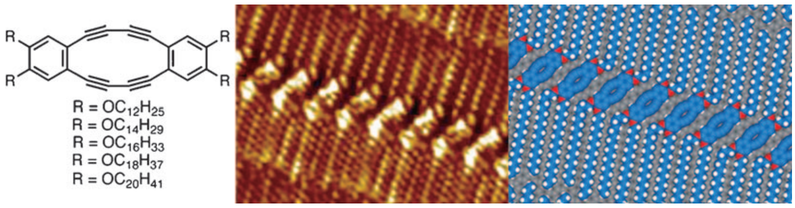


Valuable insight into the mechanism and role of the metal in the thermal decomposition of various metal amidoborane complexes has been gained by comparing the chemistry of the Mg amidoboranes with that of the Ca and Zn analogues. Bimetallic Mg amidoborane complexes (see figure) decompose differently and should be considered as more realistic models for a multi-metallic solid-state situation.

Self-Assembled Monolayers

*K. Tahara, K. Inukai, N. Hara, C. A. Johnson II, M. M. Haley, Y. Tobe** .... 8319 – 8328

Self-Assembled Monolayers of Alkoxy-Substituted Octadehydrodibenzo[12]annulenes on a Graphite Surface: Attempts at *peri*-Benzopolyacene Formation by On-Surface Polymerization

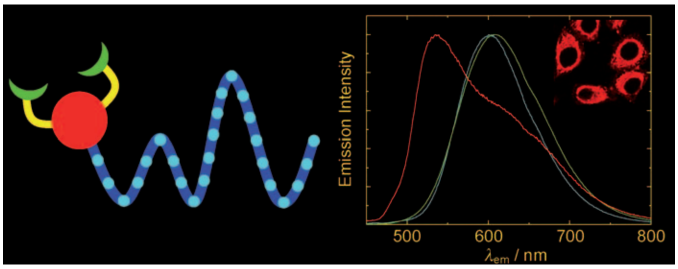


Pull yourself together: Monolayers of tetraalkoxy-substituted octadehydrobenzo[12]annulene (DBA) derivatives (see picture), which have butadiyne linkages, were studied by STM at the liquid/solid interface. The reactivity of DBA in the monolayer toward external stimuli was also investigated to assess the possibility for *peri*-benzopolyacene formation by two-dimensionally controlled polymerization on a surface.

Luminescence

*S. P.-Y. Li, H.-W. Liu, K. Y. Zhang, K. K.-W. Lo** .... 8329 – 8339

Modification of Luminescent Iridium(III) Polypyridine Complexes with Discrete Poly(ethylene glycol) (PEG) Pendants: Synthesis, Emissive Behavior, Intracellular Uptake, and PEGylation Properties



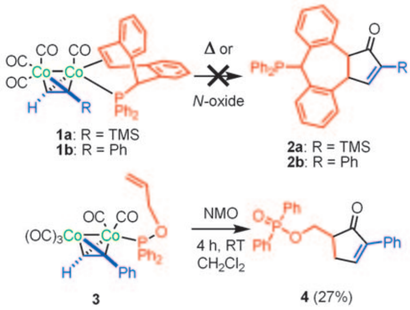
Luminescent cyclometalated iridium(III) PEG complexes have been developed as new biological probes. The PEG pendants not only perturb the photophysical properties of the complexes, but also render them to be highly water-soluble and biocompatible with extremely low cytotoxicity. One of the complexes has been functionalized with reactive aldehyde groups (see cartoon in figure), which allow the complex to serve as the first luminescent PEGylation reagent for proteins and amine-containing polymers.

Pauson–Khand Reactions

C. Ferrer, J. Benet-Buchholz, A. Riera, X. Verdaguer** .... 8340 – 8346

Phosphine–Alkene Ligands as Mechanistic Probes in the Pauson–Khand Reaction

The alkene factor: A new alkyne tetracarbonyl dicobalt complex (**1a**, see scheme) of a chelated phosphine–alkene ligand has been prepared, isolated, and characterized by X-ray crystallography. Complex **1a** serves as a structural model for an intermediate in the Pauson–Khand (PK) reaction. Despite the appropriately positioned alkene fragment for 1,2-insertion, neither thermal nor NMO activation provided the PK product. In contrast, complex **3**, featuring a terminal alkene, did provide the corresponding PK product.

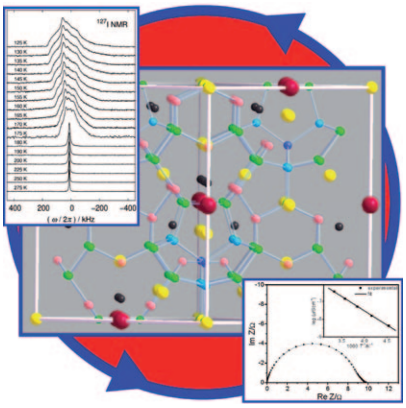


Conductivity Mechanisms

O. Pecher, S.-T. Kong, T. Goebel, V. Nickel, K. Weichert, C. Reiner, H.-J. Deiseroth, J. Maier,* F. Haarmann,* D. Zahn** ... 8347 – 8354

Atomistic Characterisation of Li$^+$ Mobility and Conductivity in Li$_{7-x}$PS$_{6-x}$I$_x$ Argyrodites from Molecular Dynamics Simulations, Solid-State NMR, and Impedance Spectroscopy

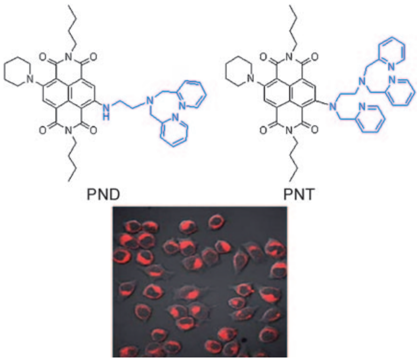
Interstitial importance: The atomistic mechanisms of Li$^+$ ion mobility/conductivity in Li$_{7-x}$PS$_{6-x}$I$_x$ argyrodites are revealed from molecular dynamics simulations, solid-state NMR, and impedance spectroscopy (see figure).



Ligand Effects

X. Lu, W. Zhu, Y. Xie, X. Li, Y. Gao, F. Li, H. Tian** .... 8355 – 8364

Near-IR Core-Substituted Naphthalenediimide Fluorescent Chemosensors for Zinc Ions: Ligand Effects on PET and ICT Channels

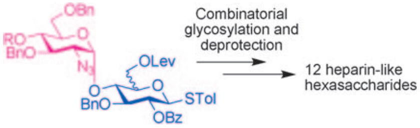


Heighten your senses! Two near-IR chemosensors for Zn^{2+}, PND and PNT, containing a novel naphthalene-diimide fluorophore are conveniently synthesized and successfully applied to the imaging of living cells (see picture). The Zn^{2+}-binding behavior and the selectivity difference between PND and PNT are investigated by absorption, fluorescence, and ^1H NMR spectroscopy.

Carbohydrates

*Z. Wang, Y. Xu, B. Yang, G. Tiruchinapally, B. Sun, R. Liu, S. Dulaney, J. Liu, X. Huang** .... 8365 – 8375

VIP **Preactivation-Based, One-Pot Combinatorial Synthesis of Heparin-like Hexasaccharides for the Analysis of Heparin–Protein Interactions**

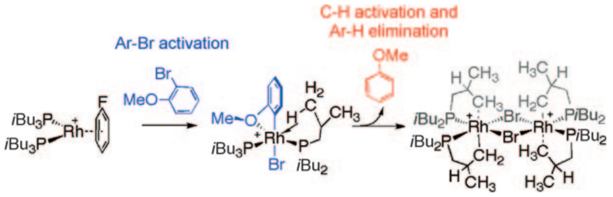


Going fast: A preactivation-based, one-pot approach allowed chemoselective glycosylation to occur without the need to fine-tune anomeric reactivities. This enabled the repeated use of the same building block set in the rapid assembly of twelve heparin-like hexasaccharides with systematically varied and precisely controlled backbone structures in a combinatorial fashion, which facilitated the understanding of the structure–activity relationship of fibroblast growth factor-2 (see scheme).

C–H Activation

N. S. Townsend, A. B. Chaplin, M. A. Naser, A. L. Thompson, N. H. Rees, S. A. Macgregor, A. S. Weller** .... 8376 – 8389

Reactivity of the Latent 12-Electron Fragment $[Rh(PiBu_3)_2]^+$ with Aryl Bromides: Aryl–Br and Phosphine Ligand C–H Activation

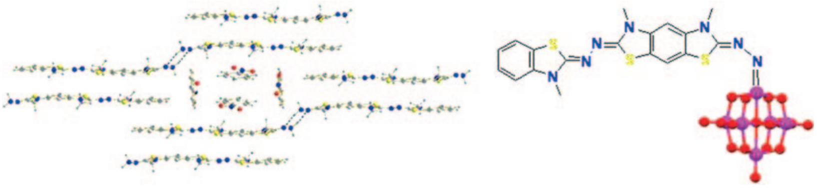


Agostic interactions: Oxidative addition of a variety of aryl bromides to the formally 12-electron Rh^I complex $[Rh(PiBu_3)_2][BAr^F_4]$ forms a number of products depending on the substrate, some of which proceed to give species that have undergone C–H activation and aryl elimination (see scheme), suggesting that they are isolated intermediates in a σ-bond metathesis reaction.

Conducting Materials

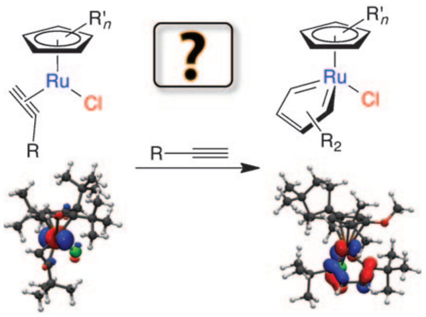
S. Gatard, S. Blanchard, B. Schollhorn, P. Gouzerh, A. Proust, K. Boubekeur** .... 8390 – 8399

VIP **Electroactive Benzothiazole Hydrazones and Their $[Mo_6O_{19}]^{2-}$ Derivatives: Promising Building Blocks for Conducting Molecular Materials**



Polyoxometalate functionalization: Synthesis of electroactive benzothiazole hydrazones has been achieved and they have been successfully coupled to $[Mo_6O_{19}]^{2-}$ to give rare examples of diazoalkane–hexamolybdates (see picture). These molecules exhibit electronic features that make these compounds very promising building blocks for the synthesis of conducting molecular materials.

Complex chemistry: Experimental and computational studies were performed to examine the reaction of [RuCl(cyclopentadienyl)] complexes with alkynes (see figure). It is shown that η^2-alkyne complexes can be isolated and that subsequent reactions are strongly dependent on steric effects.



Organometallic Chemistry

B. Dutta, B. F. E. Curchod,
P. Campomanes, E. Solari,
R. Scopelliti, U. Rothlisberger,
K. Severin* .... 8400 – 8409

Reactions of Alkynes with [RuCl(cyclopentadienyl)] Complexes: The Important First Steps

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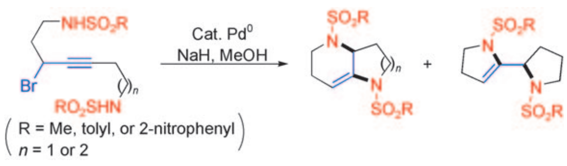

Palladium-catalyzed bis-cyclization: Propargyl bromides that have nucleophilic functional groups, such as 5-bromohept-3-yne-1,7-diamine derivatives, react with $[Pd(PPh_3)_4]$ and NaH/MeOH to selectively give fused nitrogen heterocycles that can be readily converted into the fused pyrroles in good yields (see scheme). The reaction of a 2-alkynylazetidine derivative with a catalytic amount of $[Pd(PPh_3)_4]$ proceeds under base-free conditions to give the same fused heterocycle.

Cyclization

A. Okano, K. Tsukamoto, S. Kosaka,
H. Maeda, S. Oishi, T. Tanaka,*
N. Fujii,* H. Ohno* .... 8410 – 8418

Synthesis of Fused and Linked Bicyclic Nitrogen Heterocycles by Palladium-Catalyzed Domino Cyclization of Propargyl Bromides

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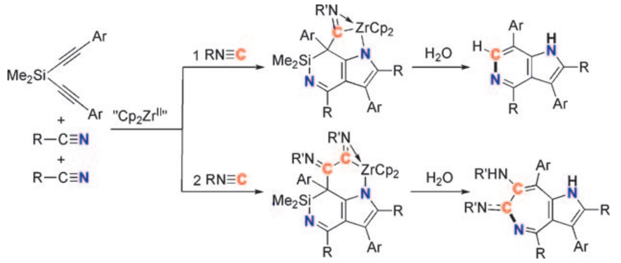

Iminoacyl–Zr intermediates: The synthesis, structures, and intramolecular cyclization of mono- and bis(iminoacyl)–Zr intermediates formed in zirconocene-mediated multicomponent coupling of silicon-tethered diynes, nitriles, and isocyanides have been investigated and directed to the efficient one-pot synthesis of 5-azaindoles and dihydropyrrolo[3,2-*c*]azepines (see scheme).

Multicomponent Reactions

S. Zhang, W.-X. Zhang,
Z. Xi* .... 8419 – 8426

Efficient One-Pot Synthesis of N-Containing Heterocycles by Multicomponent Coupling of Silicon-Tethered Diynes, Nitriles, and Isocyanides through Intramolecular Cyclization of Iminoacyl–Zr Intermediates

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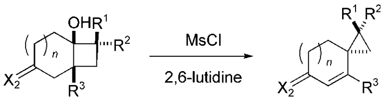
Spiro strain: An unusual ring-contraction rearrangement that gives spirocyclopropanes from fused cyclobutanols has been developed. It was found that the strain energy of the substrates derived from an additional fused ring and the stereoelectronic effect of the migrating σ bond were important factors. It is noteworthy that the rearrangement proceeds in a stereospecific manner.



Ring Contraction

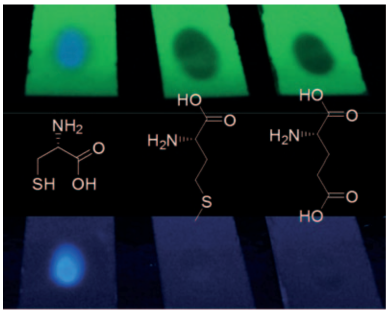
K. Takasu,* Y. Nagamoto,
Y. Takemoto* .... 8427 – 8432

Stereocontrolled Synthesis of Spiro[*n*.2]alkenes by Ring Contraction of Fused-Cyclobutanols

Biosensors

Y. Liu, Y. Yu, J. W. Y. Lam, Y. Hong,
M. Faisal, W. Z. Yuan,
*B. Z. Tang** .... 8433 – 8438

Simple Biosensor with High Selectivity and Sensitivity: Thiol-Specific Biomolecular Probing and Intracellular Imaging by AIE Fluorogen on a TLC Plate through a Thiol–Ene Click Mechanism

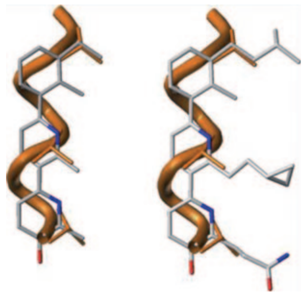


Bright SHparks! A spot of tetraphenylethene–maleimide adduct on a TLC plate is only lit up by thiol-containing biomolecules (e.g., cysteine; see figure), even in trace amounts as low as approximately 1 ppb, thus affording a convenient bioprobe with very high selectivity and sensitivity.

Peptidomimetics

G. T. Bourne, D. J. Kuster,*
G. R. Marshall .... 8439 – 8445

Synthesis of the Phenylpyridal Scaffold as a Helical Peptide Mimetic

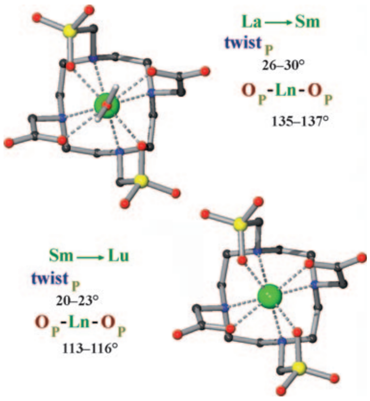


Small is beautiful: A phenylpyridal scaffold has been designed and synthesized as a helical peptide mimetic. The synthesis is concise and high yielding, allowing flexibility at the designated attachment points on the scaffold. A small library was synthesized to show the versatility of the method.

Lanthanides

M. P. C. Campello, S. Lacerda,
I. C. Santos, G. A. Pereira,
C. F. G. C. Geraldes, J. Kotek,*
P. Hermann, J. Vaněk, P. Lubal,**
V. Kubíček, É. Tóth,
*I. Santos** .... 8446 – 8465

Lanthanide(III) Complexes of 4,10-Bis(phosphonomethyl)-1,4,7,10-tetraazacyclododecane-1,7-diacetic acid (*trans*-H_6do2a2p) in Solution and in the Solid State: Structural Studies Along the Series

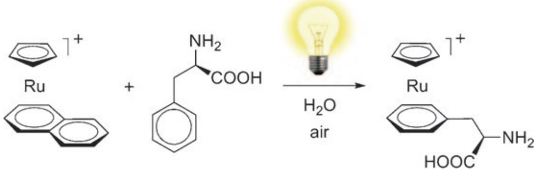


Arm twisting: An abrupt change was observed between the structural parameters of the hydrated/non-hydrated Ln^{III} complexes of *trans*-H_6do2a2p in the solid state. The coordinated water strongly changes the O_P-Ln-O_P angle and twist angle of the phosphonic/acetic pendant arms (see figure).

Compound Labeling

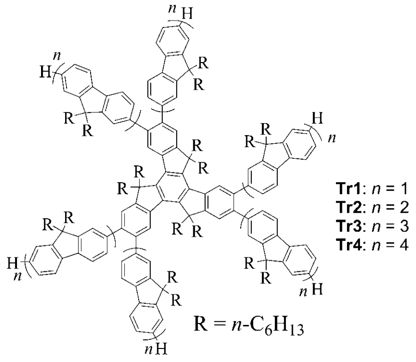
D. S. Perekalin, E. E. Karslyan,
P. V. Petrovskii, Y. V. Nelyubina,
K. A. Lyssenko, A. S. Kononikhin,
E. N. Nikolaev,
*A. R. Kudinov** .... 8466 – 8470

Simple Synthesis of Ruthenium π Complexes of Aromatic Amino Acids and Small Peptides



Simple labeling of amino acids and peptides: Ruthenium π complexes with aromatic amino acids and small peptides have been synthesized in water at room temperature (see scheme) in the presence of oxygen and concomitant biological substances (non-aromatic amino acids, sugars, and nucleotides).

Starburst macromolecules: A "homogeneous" starburst fluorene system based on a 2,3,7,8,12,13-hexaaryltruxene scaffold is presented (see scheme). Microwave heating proved to be a powerful tool throughout the synthetic procedure. The electronic properties were compared with those of corresponding linear and three-armed counterparts. The novel *ortho*-substituted, multiarm design provides materials with a nonplanar geometry that helps to define π delocalization.



Organic Semiconductors

*W.-Y. Lai, R. Xia, D. D. C. Bradley, W. Huang** .... 8471 – 8479

2,3,7,8,12,13-Hexaaryltruxenes: An *ortho*-Substituted Multiarm Design and Microwave-Accelerated Synthesis toward Starburst Macromolecular Materials with Well-Defined π Delocalization

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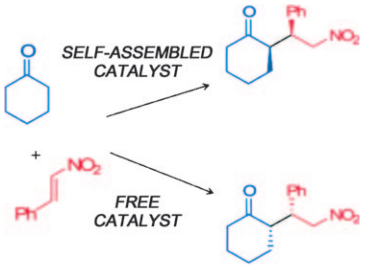
Upside down: The stereoselectivity of 1,4-conjugate addition of cyclohexanone to nitrostyrene is dramatically affected by self-assembly of the catalyst. Ultimately, self-assembly of the catalyst into a supramolecular gel yields a self-supported heterogeneous catalyst with reliable activity and stereoselectivty (see scheme).



Supramolecular Catalysis

F. Rodríguez-Llansola, J. F. Miravet, B. Escuder** .... 8480 – 8486

Supramolecular Catalysis with Extended Aggregates and Gels: Inversion of Stereoselectivity Caused by Self-Assembly

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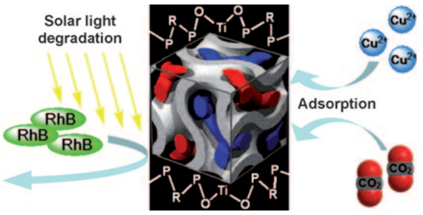
Gleaning the cube: Periodic cubic mesoporous titanium phosphonate materials with bridged organic groups inside the framework were synthesized and were further applied in the photodegradation of rhodamine B (RhB) and adsorption of heavy metal ions and CO_2 (see graphic).



Mesophases

*T.-Y. Ma, X.-Z. Lin, Z.-Y. Yuan** .... 8487 – 8494

Cubic Mesoporous Titanium Phosphonates with Multifunctionality

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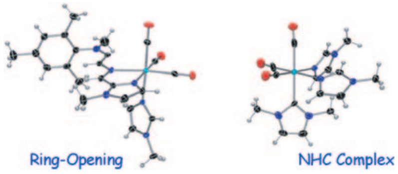
Competing families: Two different families of compounds can be obtained by the deprotonation of $[Re(CO)_3(N\text{-}RIm)_3]^+$ (*N*-RIm = *N*-alkylimidazole), depending on the nature of the alkyl substituent. Ring-opened products are obtained if there is at least one aryl group, whereas imidazol-2-yl and, after reaction with electrophiles, N-heterocyclic carbene complexes are produced otherwise (see scheme).



Ligand Effects

M. A. Huertos, J. Pérez, L. Riera,* J. Díaz, R. López** .... 8495 – 8507

Effect of the Nature of the Substituent in *N*-Alkylimidazole Ligands on the Outcome of Deprotonation: Ring Opening versus the Formation of N-Heterocyclic Carbene Complexes

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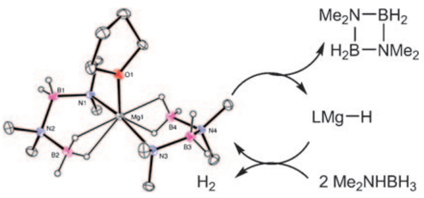
Alkaline release: Stoichiometric and catalytic reactions of alkaline earth (Mg and Ca) alkyls and amides with $Me_2NH{\cdot}BH_3$ result in the formation of the corresponding amidoborane derivatives and dehydrogenative coupling of two amine–borane fragments under mild conditions (see graphic).



Amine–Boranes

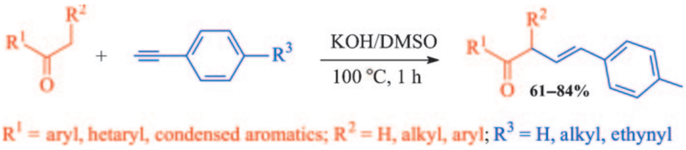
D. J. Liptrot, M. S. Hill, M. F. Mahon, D. J. MacDougall* .... 8508 – 8515

Group 2 Promoted Hydrogen Release from $NMe_2H{\cdot}BH_3$: Intermediates and Catalysis

Vinylation Reactions

B. A. Trofimov, E. Y. Schmidt, I. A. Ushakov, N. V. Zorina, E. V. Skital'tseva, N. I. Protsuk, A. I. Mikhaleva* .... 8516 – 8521

Base-Catalyzed Stereoselective Vinylation of Ketones with Arylacetylenes: A New C(sp^3)–C(sp^2) Bond-Forming Reaction

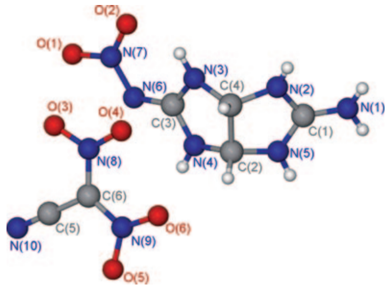


A valuable vinylation! Previously unknown C-vinylation of ketones occurs with high *E* stereoselectivity and excellent yields when alkylaryl- and alkylheteroarylketones are treated with arylacetylenes in the presence of KOH/DMSO at 100 °C. This represents a new C(sp^3)–C(sp^2) bond-forming reaction of wide scope (see scheme).

High-Density Energetic Salts

R. Wang, Y. Guo, R. Sa, J. M. Shreeve** .... 8522 – 8529

Nitroguanidine-Fused Bicyclic Guanidinium Salts: A Family of High-Density Energetic Materials

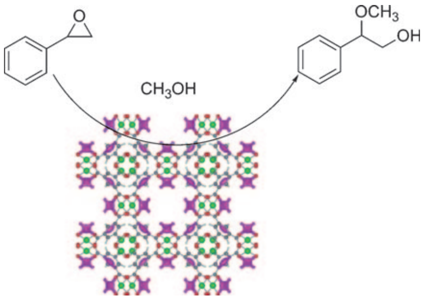


Be explosive! The nitroguanidine-fused bicyclic guanidinium energetic salts (see figure) exhibit excellent thermal stabilities, positive calculated heats of formation, high density, and promising energetic performance.

Green Chemistry

*A. Dhakshinamoorthy, M. Alvaro, H. Garcia** .... 8530 – 8536

Metal–Organic Frameworks as Efficient Heterogeneous Catalysts for the Regioselective Ring Opening of Epoxides

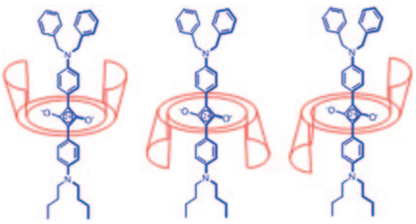


Pop goes the epoxide! An iron-based metal–organic framework has been found to efficiently catalyse the ring opening of styrene oxide with alcohols and aniline under mild reaction conditions. Methanol was found to be the most reactive alcohol (see scheme).

Self-Assembly

*M. Xue, Y.-S. Su, C.-F. Chen** .... 8537 – 8544

Isomeric Squaraine-Based [2]Pseudorotaxanes and [2]Rotaxanes: Synthesis, Optical Properties, and Their Tubular Structures in the Solid State

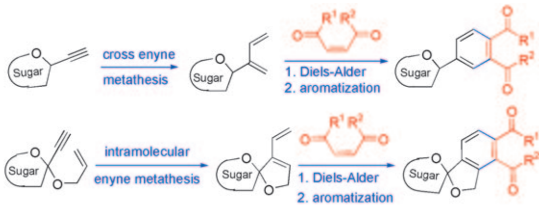


Rotate your chemistry! A series of squaraine-based isomeric [2]pseudorotaxanes and [2]rotaxanes were synthesized with triptycene-derived tetralactam macrocycles as wheels. Based on different linking modes of triptycene derivatives and different directions of nonsymmetrical squaraine insertion, three isomers of [2]rotaxanes were formed (see scheme).

Diversity-Oriented Synthesis

*A. V. Subrahmanyam, K. Palanichamy, K. P. Kaliappan** .... 8545 – 8556

Application of an Enyne Metathesis/Diels–Alder Cycloaddition Sequence: A New Versatile Approach to the Syntheses of *C*-Aryl Glycosides and Spiro-*C*-Aryl Glycosides



Simple sequence for a difficult task! A sequential enyne metathesis/Diels–Alder reaction/aromatization strategy has been developed to access the synthesis of a library of *C*-aryl and spiro-*C*-aryl glycosides (see scheme). This strategy has also been extended to the synthesis of a set of hybrids of *C*-aryl and spiro-*C*-aryl glycosides.

* Author to whom correspondence should be addressed

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