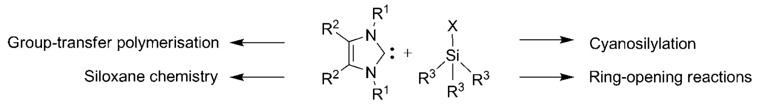
MINIREVIEWS

Organocatalysis

*M. J. Fuchter** .... 12286 – 12294

N-Heterocyclic Carbene Mediated Activation of Tetravalent Silicon Compounds: A Critical Evaluation



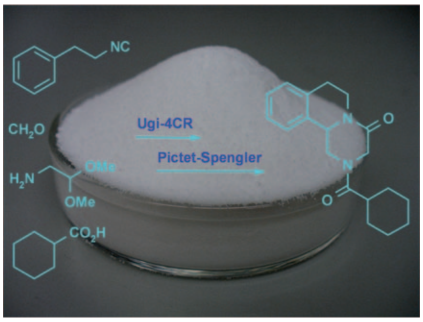
Very versatile: N-Heterocyclic carbenes (NHCs) have been reported as catalysts or initiators of a variety of organic transformations that involve silicon compounds, such as the addition of silyl pronucleophiles to a variety of electrophiles, organic and inorganic polymerisation and the reduction of CO_2 by hydrosilanes (see scheme). A summary of these developments and a discussion of the current knowledge regarding the mechanistic course of these reactions is presented.

COMMUNICATIONS

Multicomponent Reactions

*H. Cao, H. Liu, A. Dömling** .... 12296 – 12298

Efficient Multicomponent Reaction Synthesis of the Schistosomiasis Drug Praziquantel

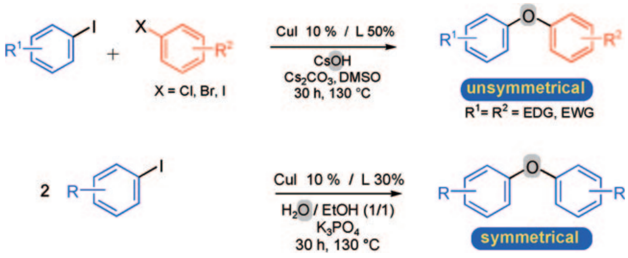


Shorter than ever: A convergent, efficient, and scalable access based on a key Ugi four-component reaction (4CR) followed by a Pictet–Spengler reaction comprises the shortest known synthesis to the schistosomiasis drug praziquantel (see scheme).

C−O Coupling

A. Tlili, F. Monnier, M. Taillefer** .... 12299 – 12302

Selective One-Pot Access to Symmetrical or Unsymmetrical Diaryl Ethers by Copper-Catalyzed Double Arylation of a Simple Oxygen Source

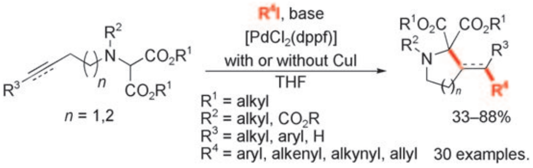


Great CO-mbination: A novel method is reported for the controlled one-pot synthesis of various symmetrical or unsymmetrical diaryl ethers by double arylation of a simple inorganic oxygen source (see scheme). This versatile and highly selective process is based on the use of a cheap and low toxicity copper catalytic system.

Nitrogen Heterocycles

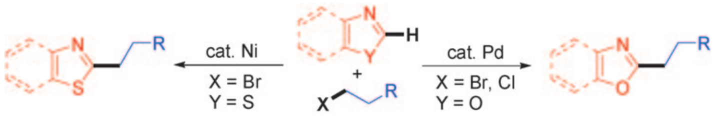
*W. Hess, J. W. Burton** ... 12303 – 12306

Palladium-Catalysed Cyclisation of *N*-Alkynyl Aminomalonates



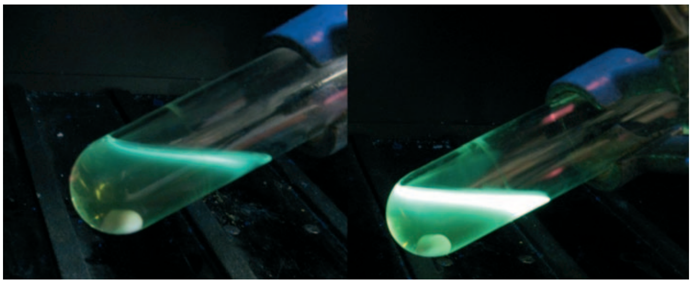
Go around in (hetero)cycles! The palladium-catalysed tandem cyclisation/coupling reaction of alkynyl- and alkenyl-substituted aminomalonates leads to highly functionalised pyrrolidines and piperidines in good yield (see scheme). The reaction allows efficient access to a broad range of synthetically valuable building blocks.

C–H Activation



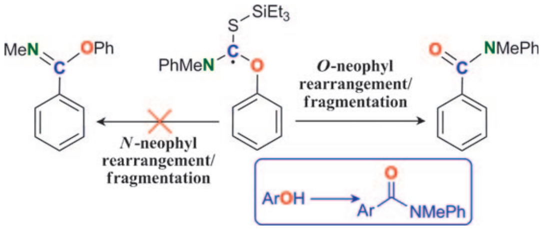
Long-ing alkyl chain: The catalytic direct C–H alkylation of azoles with unactivated alkyl bromides and chlorides is described. A palladium catalyst enables the alkylation of oxazoles, whereas a nickel one shows unique activity for thiazole. The catalyses allow a straightforward access to azole motifs bearing long, functional alkyl side chains.

Olefin Metathesis



From whose bourns no traveller returns, puzzles the will: UV/Vis, ^{19}F NMR, and fluorescence spectroscopic studies (see graphic) provide no evidence supporting the boomerang mechanism in Grubbs–Hoveyda complexes, which is the return of the isopropoxy styrene as a benzylidene ether ligand following its release during catalyst initiation.

Radical Reactions

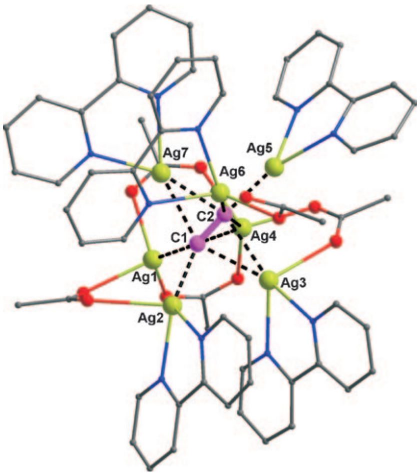


Radical merry-go-round: A highly efficient metal-free transformation of phenols into benzamides is designed through one-step conversion of phenols to aryl thiocarbamates and a subsequent radical addition/rearrangement/fragmentation cascade. Computational analysis fully rationalizes the experimentally observed selectivity. Despite the possible competition from N–C fragmentation and *N*-neophyl rearrangement, the transformation exclusively follows the most kinetically and thermodynamically favored *O*-neophyl rearrangement path.

Cluster Compounds

*H.-B. Wu, Z.-J. Huang, Q.-M. Wang** .... 12321 – 12323

Unprecedented Solution-Stable Silver(I) Ethynediyl Clusters

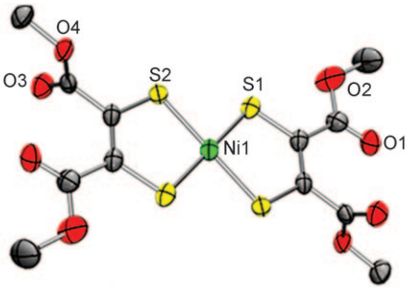


Rise of the silver surfer: A novel solution-stable silver ethynediyl complex $[Ag_7(C_2)(CF_3CO_2)_5(bpy)_5]\cdot MeCN\cdot 0.5\,MeOH$ (bpy = 2,2′-bipyridine) was prepared by reacting $Me_3SiC{\equiv}CH$ with $[Ag(bpy)CF_3CO_2]$ in methanol (see figure). This complex represents the first example of a solution-stable silver ethynediyl cluster, and it is yellow emissive in MeCN/MeOH at 77 K.

H_2 Evolution

*A. Begum, G. Moula, S. Sarkar** .... 12324 – 12327

A Nickel(II)–Sulfur-Based Radical-Ligand Complex as a Functional Model of Hydrogenase



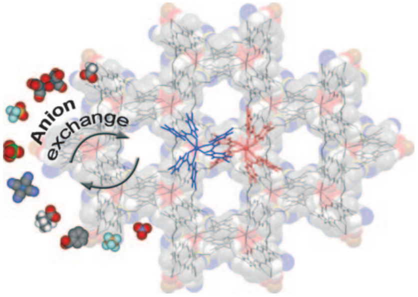
Better than nature! A nickel(II) dithiolene complex $[Ni^{II}(L^{2-})(L^{-\bullet})][PPh_4]$ (**1**; see figure; L = 1,2-dicarbomethoxyethylene dithiolate) electrocatalyzes hydrogen evolution at the lowest achievable reduction potential (E_p^{red}, −0.69 V) in CH_3CN and also in aqueous medium (E_p^{red}, −0.71 V) to date. Compound **1** shows strikingly similar EPR and reduction potential values to those observed with native Ni-containing hydrogenases.

FULL PAPERS

Heterometallic Networks

L. Carlucci, G. Ciani, S. Maggini, D. M. Proserpio, M. Visconti* .... 12328 – 12341

Heterometallic Modular Metal–Organic 3D Frameworks Assembled via New Tris-β-Diketonate Metalloligands: Nanoporous Materials for Anion Exchange and Scaffolding of Selected Anionic Guests

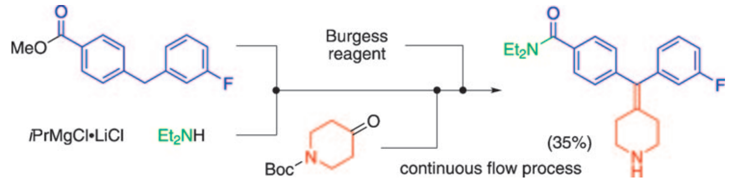


Remarkably always the same framework! Novel tris-chelate β-diketonate metalloligands were reacted with AgX salts to give more than 20 heterometallic networks of the type $[M^{III}\mathbf{L}_3Ag_3]X_3$ and $[M^{II}\mathbf{L}_3Ag_3]X_2$, all exhibiting the same framework structure, in spite of the different metal nodes, ionic charges and X^- counterions. These nanoporous networks display large 1D channels containing the anions, which are easily exchanged with many anionic species (see figure).

Solid-Phase Synthesis

*Z. Qian, I. R. Baxendale, S. V. Ley** .... 12342 – 12348

A Continuous Flow Process Using a Sequence of Microreactors with In-line IR Analysis for the Preparation of *N,N*-Diethyl-4-(3-fluorophenylpiperidin-4-ylidenemethyl)benzamide as a Potent and Highly Selective δ-Opioid Receptor Agonist

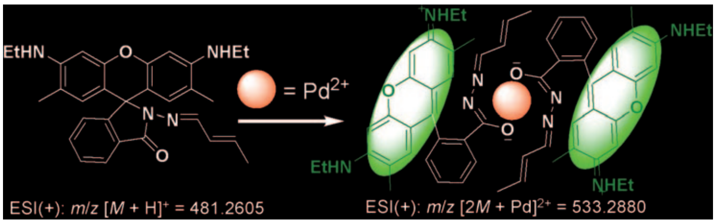


A four-step flow synthesis of a potent δ-opioid receptor agonist was developed (see scheme), using a continuation of pumping devices in combination with cartridges packed with appropriate scavengers to effect clean delivery of the product. We have also reported the use of in-line ReactIR monitoring to synchronise pumping of a late input stream to coordinate reactive components.

Fluorescent Probes

*H. Li, J. Fan, F. Song, H. Zhu, J. Du, S. Sun, X. Peng** .... 12349 – 12356

Fluorescent Probes for Pd^{2+} Detection by Allylidene–Hydrazone Ligands with Excellent Selectivity and Large Fluorescence Enhancement

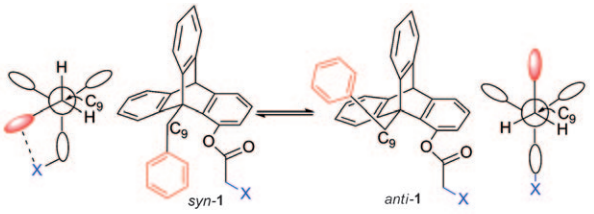


Sensitive and selective: Two fluorescent probes for Pd^{2+} have been developed. The results show that conjugated allylidene–hydrazone has much better affinity toward Pd^{2+}, and consequently better selectivity over other metal ions (especially platinum-group elements) than the unconjugated allyl–hydrazine (see graphic).

Noncovalent Interactions

B. W. Gung, B. U. Emenike, M. Lewis, K. Kirschbaum* .... 12357 – 12362

Quantification of CH⋅⋅⋅π Interactions: Implications on How Substituent Effects Influence Aromatic Interactions



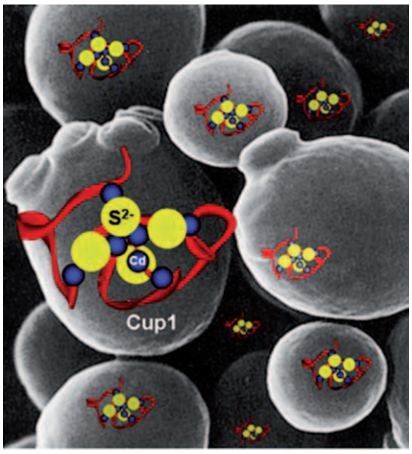
A predominant CH⋅⋅⋅π interaction was found to control the conformational preference of model compounds **1a**–**g**. Despite the predominance of the CH⋅⋅⋅π interaction in compounds **1a**–**g**, a Hammett plot displays a fairly straight line for the substituent effect. These results show that when using Hammett plots in a simplified model system, a system designed to study the effect of X⋅⋅⋅π interactions could capture the X−H⋅⋅⋅π interaction instead.

Metalloproteins

*R. Orihuela, F. Monteiro, A. Pagani, M. Capdevila, S. Atrian** 12363 – 12372

Evidence of Native Metal–S^{2-}–Metallothionein Complexes Confirmed by the Analysis of Cup1 Divalent-Metal-Ion Binding Properties

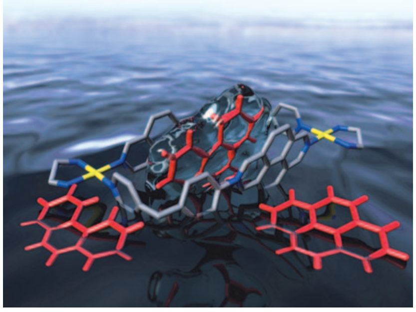
Definitive evidence that sulfide ligands are also constituents of native metal–metallothionein (MT) complexes (see picture) is provided. Therefore, this investigation goes beyond the study of a particular MT and complements previous results about the presence of sulfide moieties in recombinant MT samples. A new point of view on the interaction between copper thioneins and divalent metal ions is delineated.



Supramolecular Chemistry

V. Blanco, M. D. García, A. Terenzi, E. Pía, A. Fernández-Mato, C. Peinador, J. M. Quintela** .... 12373 – 12380

Complexation and Extraction of PAHs to the Aqueous Phase with a Dinuclear Pt^{II} Diazapyrenium-Based Metallacycle

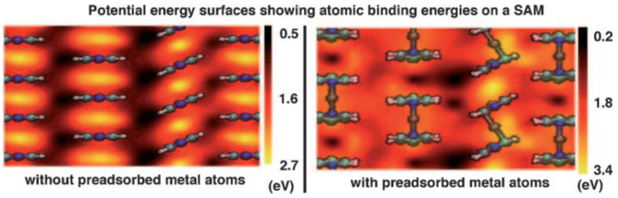


SuPAH extraction! New metallacycles have been synthesized by self-assembly between a 2,7′-diazapyrenium-based ligand and Pd^{II} and Pt^{II} complexes. The inclusion complexes between the metallacycles and polycyclic aromatic hydrocarbons (PAHs) in CD_3CN and D_2O were studied. The structures of complexes with pyrene, phenanthrene, and triphenylene were confirmed by single-crystal X-ray crystallography (see graphic). The estimated association constants in water correlate with the hydrophobicity of the PAH.

Self-Assembled Monolayers

*J. A. Keith, T. Jacob** ..... 12381 – 12386

Atomic-Level Elucidation of the Initial Stages of Self-Assembled Monolayer Metallization and Nanoparticle Formation

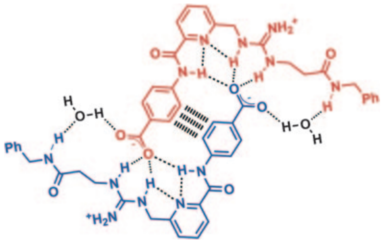


Mind the gap: We report first-principle quantum mechanics simulations depicting the initial stages of self-assembled monolayer (SAM) metallization. Stepwise mechanisms whereby pre-adsorbed metal atoms induce SAM relaxation in turn cause a much smoother potential energy surface that permits facile diffusions leading to nanoparticle growth (see picture).

Self-Assembly

*M. Irfan Ashiq, B. F. Tesfatsion, F. Gaggini, S. Dixon, J. D. Kilburn** .... 12387 – 12397

Dimeric Self-Assembly of Pyridyl Guanidinium Carboxylates in Polar Solvents

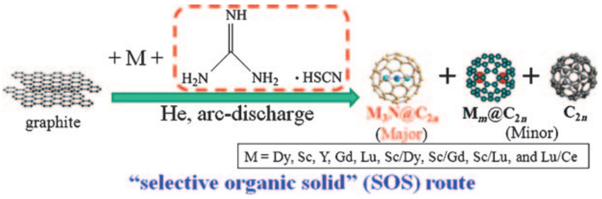


Pairing up: A dimeric self-assembly of pyridyl guanidinium carboxylates (see scheme) has been conceived as a simple model for characterisation of intermolecular interactions between a variable tethering region. We describe the synthesis and study of the self-assembly in H_2O/DMSO solvent systems using dilution microcalorimetry and ^1H NMR spectroscopy.

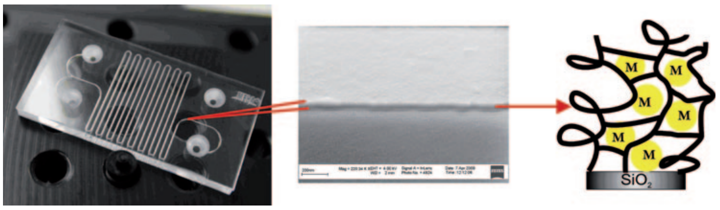
Fullerenes

S. Yang, L. Zhang, W. Zhang, L. Dunsch** .... 12398 – 12405

A Facile Route to Metal Nitride Clusterfullerenes by Using Guanidinium Salts: A Selective Organic Solid as the Nitrogen Source



An SOS for NCFs: A new “selective organic solid” (SOS) route for the facile synthesis of metal nitride clusterfullerenes (NCFs) by using guanidinium thiocyanate as the new nitrogen source (see scheme) has been developed. It promises both the high selectivity of NCFs and the high reproducibility of fullerene yield.



Nanoparticle catalysis in microreactors: Easily tuneable brush-gel/metal-nanoparticle hybrid systems in microchannels are very efficient in heterogeneously catalyzed reactions in continuous flow microreactors (see graphic). The number of nanoparticles formed in situ can be fine-tuned, since the growth of the brush can be regulated.

Heterogeneous Catalysis

F. Costantini, E. M. Benetti, R. M. Tiggelaar, H. J. G. E. Gardeniers, D. N. Reinhoudt, J. Huskens, G. J. Vancso, W. Verboom** .... 12406 – 12411

A Brush-Gel/Metal-Nanoparticle Hybrid Film as an Efficient Supported Catalyst in Glass Microreactors

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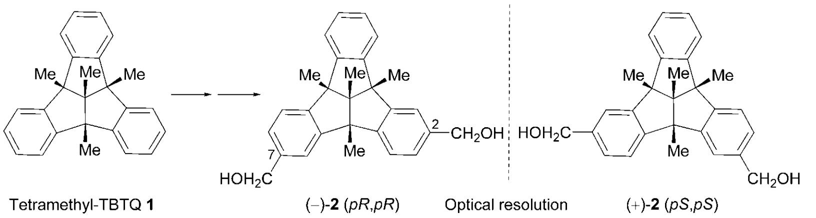

Get versatile! Based on a remarkably regioselective bis-formylation of tribenzotriquinacene **1**, enantiomerically pure difunctionalized tribenzotriquinacene (TBTQ) derivatives, such as (−)-**2** and (+)-**2** were synthesized for the first time and their optical properties and absolute configuration were determined. The corresponding C_s-symmetrical isomers, led to several novel TBTQ-dithiacyclophanes, including the first "dimeric" TBTQ-based cyclophane.

Synthetic Chemistry

T. Wang, Q.-Q. Hou, Q.-F. Teng, X.-J. Yao, W.-X. Niu, X.-P. Cao, D. Kuck** .... 12412 – 12424

Tribenzotriquinacenes Based on Regioselective Bis-formylation: Optical Resolution and Absolute Configuration of Inherently Chiral Derivatives and Synthesis of the First Cyclophane-Type Tribenzotriquinacene Dimers

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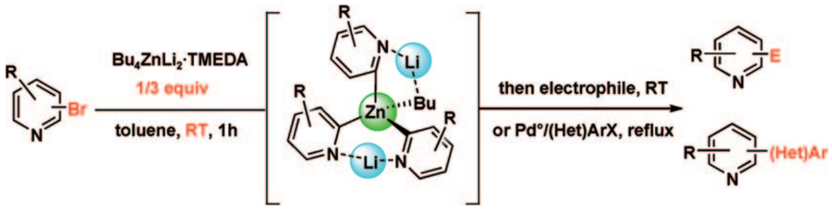

Mild zincation! nBu$_4$ZnLi$_2$·TMEDA (in substoichiometric amounts) promoted efficient and chemoselective room-temperature bromine–metal exchange of a range of bromopyridines (see scheme). DFT calculations strongly supported the formation of a stabilized tripyridylzincate, which could be reacted with electrophiles or be directly involved in palladium-catalyzed cross-coupling reactions.

Tetraorganozincates

*N. T. T. Chau, M. Meyer, S. Komagawa, F. Chevallier, Y. Fort, M. Uchiyama, F. Mongin, P. C. Gros** . . 12425 – 12433

Homoleptic Zincate-Promoted Room-Temperature Halogen–Metal Exchange of Bromopyridines

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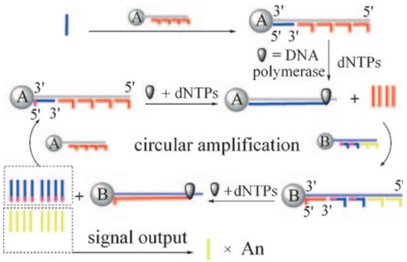
DNA—A cog in the machine! An autonomous bio-barcode DNA machine that is driven by template-dependent DNA replication is developed for exponential DNA amplification (see picture). Combined with a sensing part based on a DNA aptamer, the DNA machine can be further applied in the amplified detection of small molecules.



DNA Recognition

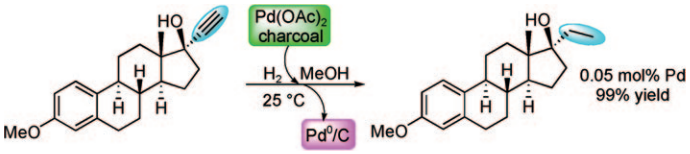
*H. Zhang, C. Fang, S. Zhang** .... 12434 – 12439

An Autonomous Bio-barcode DNA Machine for Exponential DNA Amplification and Its Application to the Electrochemical Determination of Adenosine Triphosphate

Supported Catalysts

*F.-X. Felpin,**
E. Fouquet .... 12440 – 12445

A Useful, Reliable and Safer Protocol for Hydrogenation and the Hydrogenolysis of *O*-Benzyl Groups: The In Situ Preparation of an Active Pd^0/C Catalyst with Well-Defined Properties

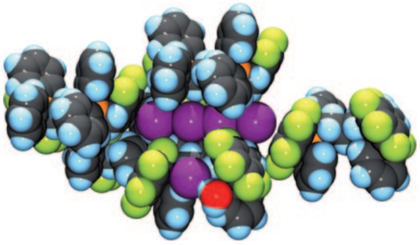


Pd^0/C: It's a kind of magic! A sustainable, simple and highly reproducible protocol for the hydrogenation of alkenes and alkynes (see scheme) and for the hydrogenolysis of *O*-benzyl ethers has been developed with an in situ generated Pd^0/C catalyst. The homemade Pd^0/C catalyst allows mild reaction conditions (25 °C, 1 atm H$_2$) and low catalyst loading (as low as 0.025 mol %), without any contamination of the product by palladium residues (<4 ppb).

Anion–Pi Interactions

M. Müller, M. Albrecht, V. Gossen, T. Peters, A. Hoffmann, G. Raabe, A. Valkonen,*
*K. Rissanen** .... 12446 – 12453

Anion–π Interactions in Salts with Polyhalide Anions: Trapping of I$_4^{2-}$

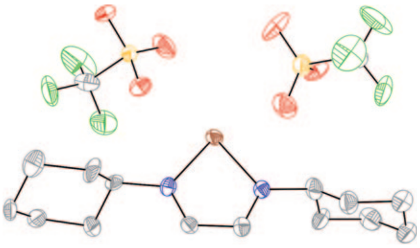


Sheltered and tranquil: Br$_3^-$, I$_3^-$, and I$_4^{2-}$ are incorporated into different ammonium and phosphonium salts, in which they show, for example, anion–π interactions with the electron-deficient C$_6$F$_5$ groups of the cations. Theoretical calculations indicate that I$_4^{2-}$ is highly unstable, but is stabilized in the obtained crystals. A bis-phosphonium salt incorporating I$^-$ and I$_4^{2-}$ (C gray, F green, H light blue, I purple, P orange) is shown here.

N Ligands

J. L. Dutton,
*P. J. Ragogna** .... 12454 – 12461

Dicationic Tellurium Analogues of the Classic N-Heterocyclic Carbene

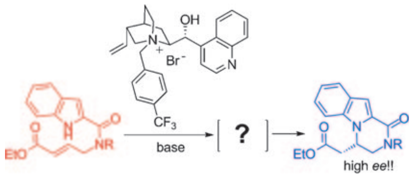


Carbene analogues: Compounds based on an unsaturated diimine ligand bear two lone pairs of electrons about the central element and can be considered structural mimics of N-heterocyclic carbenes (NHCs; see figure). Heterocycles centered about a saturated diamine carry one stereochemically active lone pair of electrons on tellurium, and are therefore isovalent as well as isostructural to NHCs.

Phase-Transfer Catalysis

M. Bandini, A. Bottoni, A. Eichholzer, G. P. Miscione,**
M. Stenta .... 12462 – 12473

Asymmetric Phase-Transfer-Catalyzed Intramolecular N-Alkylation of Indoles and Pyrroles: A Combined Experimental and Theoretical Investigation



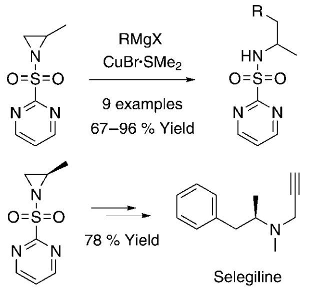
Union is strength: A combined computational and experimental investigation has shed light on a network of weak interactions responsible for the high stereochemical translation in the phase-transfer-catalyzed intramolecular N-alkylation of indoles (see figure).

Protecting Groups

*J. Bornholdt, J. Felding, R. P. Clausen, J. L. Kristensen** .... 12474 – 12480

Ring Opening of Pymisyl-Protected Aziridines with Organocuprates 💻

Easy on—easy off: The pymisyl group is introduced as a new protecting group for the activation of aziridines towards ring opening with organocuprates (see scheme). It is readily removed under very mild conditions with thiolates. The versatility of the approach is illustrated in a new synthesis of Selegiline, a drug marketed for the treatment of Parkinson's disease.

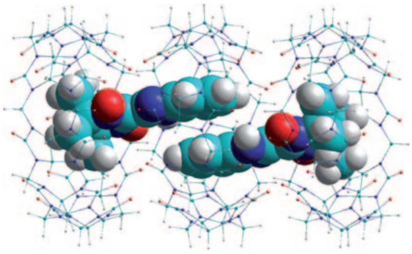


Inclusion Compounds

*E. V. Peresypkina, V. P. Fedin, V. Maurel, A. Grand, P. Rey, K. E. Vostrikova** .... 12481 – 12487

Inclusion of a Nitronyl Nitroxyl Radical and Its Hydrochloride in Cucurbit[8]uril 💻

Paramagnetic inclusion complexes: Recognition of 2-(2-benzimidazolyl)-4,4,5,5-tetramethylimidazolidinyl-3-oxide-1-oxy by cucurbit[8]uril has been investigated. The hydrochloride of this nitronyl nitroxide radical forms a 1:1 complex, whereas the neutral nitronyl nitroxide forms a supramolecular species involving three hosts and two radical guests (see figure; C cyan, H white, N red, O blue) with a triplet ground spin state.



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* Author to whom correspondence should be addressed

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