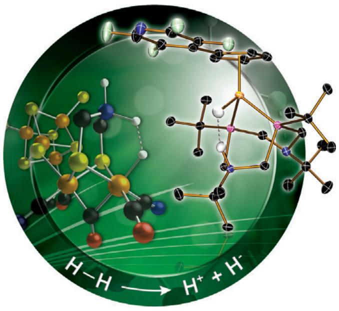
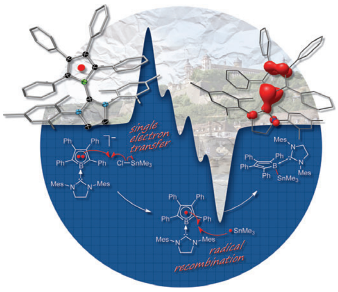
The hydroazidation of unactivated alkynes ...

... is described by X. Bi and co-workers in their Communication on page 5305 ff. Silver catalysis enabled the chemo- and regioselective transformation of ethynyl carbinols into vinyl azides. A wide variety of 2-azidoallyl alcohols were obtained in good to excellent yields. The synthetic utility of 2-azidoallyl alcohols was demonstrated by further transformations into NH aziridines.

Heterolytic H_2 Cleavage

A synthetic model complex of an iron hydrogenase was used by Bullock et al. on page 5300 ff. to investigate the heterolytic cleavage of H_2 using neutron diffraction.



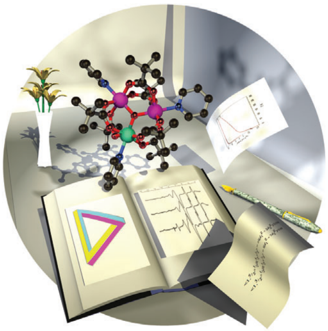


Boron Radicals

A borolyl anion undergoes single-electron-transfer (SET) processes in its reaction with triorganotetrel halides. In their Communication on page 5453 ff., H. Braunschweig and co-workers describe the first isolation of a neutral borole radical along with far-reaching synthetic implications.

Magnetic Anisotropy

E. J. L. McInnes et al. show in their Communication on page 5310 ff. that the antisymmetric component of the electronic exchange interaction (also known as Dzyaloshinski–Moriya exchange) is responsible for the large magnetic anisotropy in the $S=5/2$ ground state of a trimetallic complex.



How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

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Fax: (+49) 6201–606-331
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Service

Author Profile

“In a spare hour, I go hiking in the forest and mountains. If I could be a piece of lab equipment, I would be a very stable and tunable femtosecond laser …”
This and more about Dongho Kim can be found on page 5240.

News

S. Perrier

K. Prassides

P. J. Skabara

R. V. Ulijn

J. S. Dickschat

Books

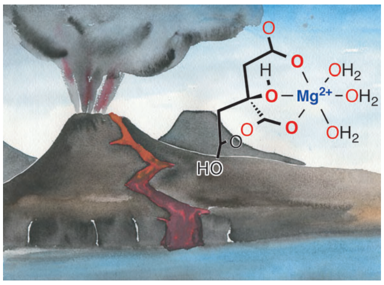
Highlights

Prebiotic Chemistry

U. F. Müller,* Y. Tor* ______ **5245 – 5247**

Citric Acid and the RNA World

RNA world: The chelation of magnesium ions by citric acid prevents the magnesium-induced aggregation of lipid vesicles and RNA degradation while promoting nonenzymatic RNA oligomerization. These findings suggest a unique role for this simple organic acid in supporting key processes in RNA world organisms.

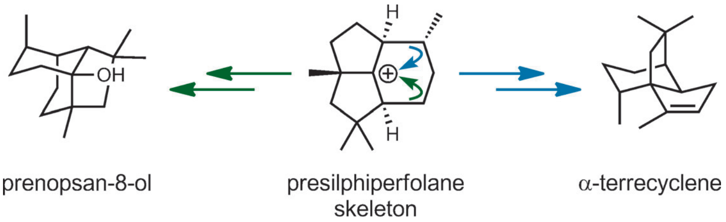


Minireviews

Natural Product Synthesis

A. Y. Hong, B. M. Stoltz* ___ **5248 – 5260**

Biosynthesis and Chemical Synthesis of Presilphiperfolanol Natural Products



All in the family: The presilphiperfolane skeleton is an important intermediate in the diverging biosynthetic pathways leading to numerous sesquiterpene natural products. Research in natural products, biosynthetic, and computational chemistry has provided much insight into the major skeletal rearrangement mechanisms. Advances in synthetic organic chemistry have enabled access to several members of the presilphiperfolanol family by total synthesis and contributed to current understanding.

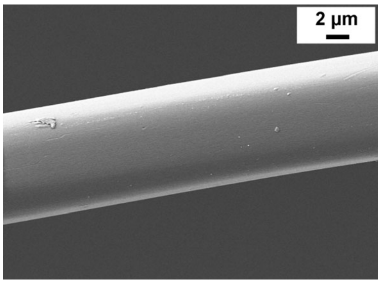
Reviews

Materials Science

E. Frank, L. M. Steudle, D. Ingildeev,
J. M. Spörl,
M. R. Buchmeiser* ________ **5262 – 5298**

Carbon Fibers: Precursor Systems, Processing, Structure, and Properties

Strand and deliver: Different precursor systems for the synthesis of carbon fibers, their processing, and the properties of the resulting carbon fibers with respect to the precursor used as well as the latest developments in alternative precursor systems are presented.



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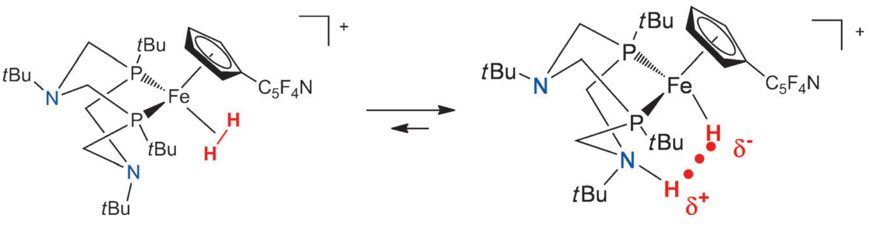
Heterolytic H_2 Cleavage

T. Liu,* X. Wang, C. Hoffmann,
D. L. DuBois,
R. M. Bullock* ——— 5300 – 5304

Heterolytic Cleavage of Hydrogen by an Iron Hydrogenase Model: An Fe-H···H-N Dihydrogen Bond Characterized by Neutron Diffraction



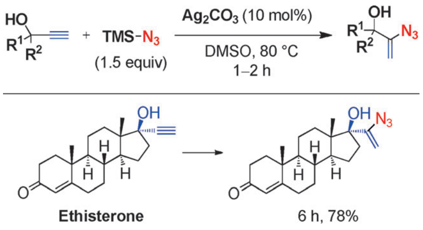
Caught in the act: The addition of H_2 to a synthetic iron complex containing a pendant amine (a model complex for [FeFe] hydrogenase) leads to facile heterolytic cleavage of H_2. Neutron diffraction indicates a very short H···H bond distance of 1.489(10) Å in the Fe-H···H-N complex, thus providing a glimpse of how the H–H bond is oxidized in hydrogenase enzymes.

Frontispiece

Hydroazidation

Z. Liu, J. Liu, L. Zhang, P. Liao, J. Song,
X. Bi* ——— 5305 – 5309

Silver(I)-Catalyzed Hydroazidation of Ethynyl Carbinols: Synthesis of 2-Azidoallyl Alcohols



Azides and aziridines: The hydroazidation of unactivated alkynes by means of silver catalysis is described. A variety of ethynyl carbinols are capable of reacting with trimethylsilyl azide to produce 2-azidoallyl alcohols in good to excellent yields. The synthetic utility of 2-azidoallyl alcohols was demonstrated by further conversion into NH aziridines.

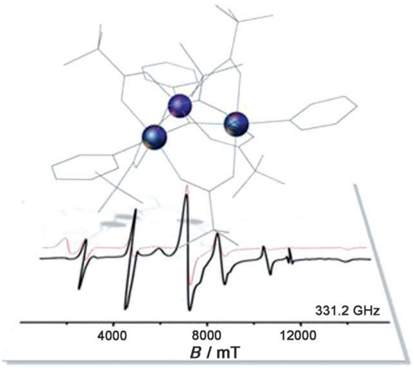
Front Cover

Magnetic Anisotropy

S. A. Magee, S. Sproules, A.-L. Barra,
G. A. Timco, N. F. Chilton, D. Collison,
R. E. P. Winpenny,
E. J. L. McInnes* ——— 5310 – 5313

Large Zero-Field Splittings of the Ground Spin State Arising from Antisymmetric Exchange Effects in Heterometallic Triangles

Zeroing in: By using [Ru$^{III}_2$Mn^{II}(O)(tBuCO$_2$)$_6$(py)$_3$] as an example, antisymmetric exchange effects have been shown to lead to very large spin ground-state zero-field splittings in polymetallic complexes. The zero-field splitting of the $S = {}^5/_2$ ground state of the heterometallic oxo-centered triangle has been measured as $D = 3\ \text{cm}^{-1}$, an order of magnitude larger than found for the {Fe$_2$Mn} analogue.

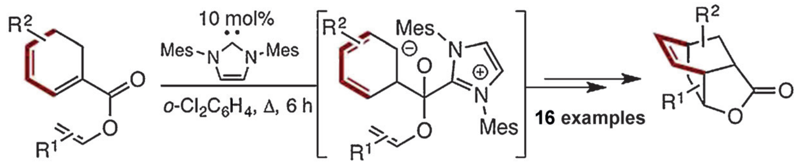


Back Cover

NHC Catalysis

M. Kowalczyk,
D. W. Lupton* ——— 5314 – 5317

Cascade Olefin Isomerization/Intramolecular Diels–Alder Reaction Catalyzed by N-Heterocyclic Carbenes

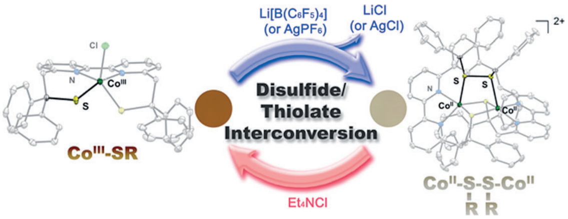


NHC-catalyzed cascade: The addition of an N-heterocyclic carbene (NHC) to the carbonyl group of an α,β,γ,δ-unsaturated enol ester affords a hemiacetal azolium intermediate that enables a cascade olefin isomerization/Diels–Alder reaction. Preliminary studies into the utility of the products using reductive and oxidative cleavage gave substrates for potential use in the synthesis of complex targets.

Bioinorganic Chemistry

M. Gennari,* B. Gerey, N. Hall, J. Pécaut, M.-N. Collomb, M. Rouzières, R. Clérac, M. Orio, C. Duboc* ______ 5318 – 5321

A Bio-Inspired Switch Based on Cobalt(II) Disulfide/Cobalt(III) Thiolate Interconversion

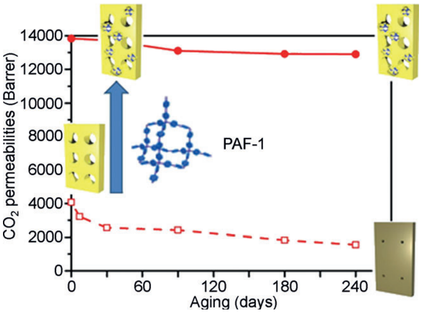


A switchable Co^{II}_2 disulfide/Co^{III} thiolate system (see scheme; filled circles show the color change) is stable under aerobic conditions. It offers the chance to understand the disulfide/thiolate interconversion supported by transition-metal ions, which is proposed to be involved in various fundamental biological processes.

Anti-Aging Membranes

C. H. Lau, P. T. Nguyen, M. R. Hill,* A. W. Thornton, K. Konstas, C. M. Doherty, R. J. Mulder, L. Bourgeois, A. C. Y. Liu, D. J. Sprouster, J. P. Sullivan, T. J. Bastow, A. J. Hill, D. L. Gin, R. D. Noble* ______ 5322 – 5326

Ending Aging in Super Glassy Polymer Membranes

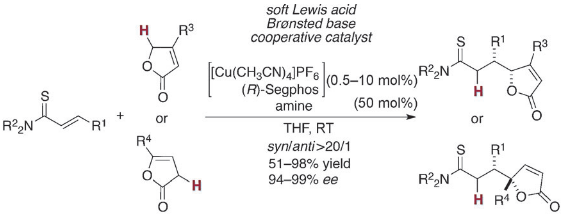


Forever young: Like stringed beads, polymer chains of a permeable membrane are intercalated within the pores of PAF-1 particles thus inhibiting polymer chain relaxation and stopping aging. PAF-1 incorporation also drastically enhanced gas permeabilities (see picture).

Asymmetric Catalysis

L. Yin, H. Takada, S. Lin, N. Kumagai,* M. Shibasaki* ______ 5327 – 5331

Direct Catalytic Asymmetric Vinylogous Conjugate Addition of Unsaturated Butyrolactones to α,β-Unsaturated Thioamides



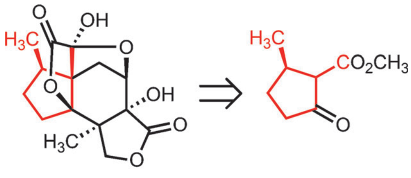
Soft spot: Soft Lewis acid/Brønsted base cooperative catalysts have enabled the title reaction of α,β- and β,γ-unsaturated butyrolactones with perfect atom economy. When using α-angelica lactone and its derivatives as pronucleophiles, a 0.5 mol % catalyst loading was sufficient to complete the reaction to construct consecutive tri- and tetrasubstituted stereogenic centers in a highly diastereo- and enantioselective fashion.

Natural Products

D. A. Siler, J. D. Mighion, E. J. Sorensen* ______ 5332 – 5335

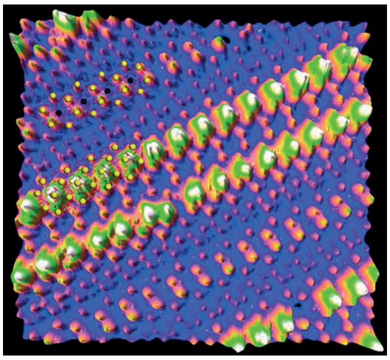
An Enantiospecific Synthesis of Jiadifenolide

Establishing the framework: A Robinson annulation, van Leusen homologation, and a desymmetrizing C–H oxidation enabled an enantiospecific synthesis of the neurotrophic natural product jiadifenolide. From a pulegone-derived building block, a key propellane intermediate was constructed through the use of simple reagents in a highly diastereoselective fashion. A short series of oxidations of this tricylic framework allowed progression to the natural product.



jiadifenolide

Positively active: Copper oxide based structures were the first that could catalyze the oxidation of CO at room temperature. Their deactivation, however, is facile, because the required Cu^+ state cannot be preserved under the reaction conditions. The addition of the right amount of titanium leads to mixed $CuTiO_x$ films that are thermally and chemically stable and more active CO oxidation catalysts than pure copper oxide materials.

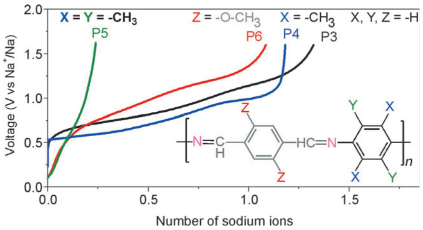


Mixed-Oxide Catalysts

A. E. Baber, X. Yang, H. Y. Kim, K. Mudiyanselage, M. Soldemo, J. Weissenrieder, S. D. Senanayake, A. Al-Mahboob, J. T. Sadowski, J. Evans, J. A. Rodriguez, P. Liu, F. M. Hoffmann, J. G. Chen, D. J. Stacchiola* **5336 – 5340**

Stabilization of Catalytically Active Cu^+ Surface Sites on Titanium–Copper Mixed-Oxide Films

---



Energy storage: Simple polymeric Schiff bases insert sodium ions at low potential with high capacities. More than one sodium ion can be reversibly stored per C=N bond in polymeric Schiff bases (see picture) with the active unit −N=CH−Ar−HC=N− that contains ten π electrons.

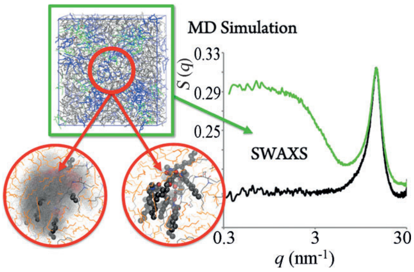
Sodium-Ion Battery

E. Castillo-Martínez, J. Carretero-González, M. Armand* **5341 – 5345**

Polymeric Schiff Bases as Low-Voltage Redox Centers for Sodium-Ion Batteries

---

A terrific team: The ill-defined self-aggregation of metal-ion extractants in oils was determined by using a combination of molecular-dynamics simulation and small-/wide-angle X-ray scattering (SWAXS) techniques (see picture). In this way, it was possible to quantitatively describe the molecular and supramolecular organization of the extractant in the organic phase at a wide range of concentrations.



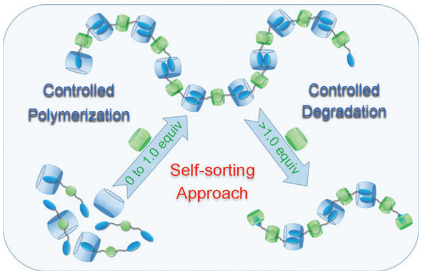
Extractant Aggregation

G. Ferru, D. Gomes Rodrigues, L. Berthon, O. Diat, P. Bauduin, P. Guilbaud* **5346 – 5350**

Elucidation of the Structure of Organic Solutions in Solvent Extraction by Combining Molecular Dynamics and X-ray Scattering

---

Got it under control: A method in which supramolecular polymerization is controlled through self-sorting is reported. The *p*-phenylene (green circles) and naphthalene (blue ovals) moieties of the bifunctional monomer are selectively recognized by cucurbit[7]uril (green barrels) and cucurbit[8]uril (blue barrels), respectively. The processes of polymerization and degradation can be controlled by tuning the cucurbit[7]uril content.



Supramolecular Polymers

Z. H. Huang, L. L. Yang, Y. L. Liu, Z. Q. Wang, O. A. Scherman, X. Zhang* **5351 – 5355**

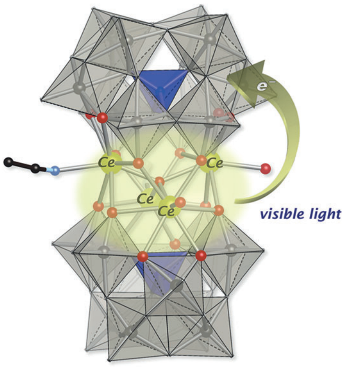
Supramolecular Polymerization Promoted and Controlled through Self-Sorting

Photoredox Catalysis

K. Suzuki, F. Tang, Y. Kikukawa,
K. Yamaguchi, N. Mizuno* _ **5356 – 5360**

Visible-Light-Induced Photoredox Catalysis with a Tetracerium-Containing Silicotungstate

Cerium, silicon, tungsten: Intramolecular Ce^{III}-to-POM(W^{VI}) charge transfer is observed when the tetranuclear cerium(III)-containing silicotungstate CePOM is irradiated with visible light ($\lambda > 400$ nm; POM = polyoxometalate). This enabled the photocatalytic oxidative dehydrogenation of primary and secondary amines as well as the α-cyanation of tertiary amines in the presence of O_2 (1 atm) as the sole oxidant.

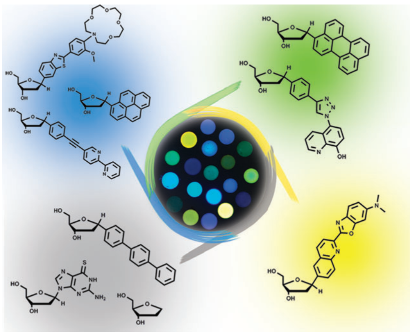


Fluorescence Sensing

L. H. Yuen, R. M. Franzini, S. Wang,
P. Crisalli, V. Singh, W. Jiang,
E. T. Kool* ______________ **5361 – 5365**

Pattern-Based Detection of Toxic Metals in Surface Water with DNA Polyfluorophores

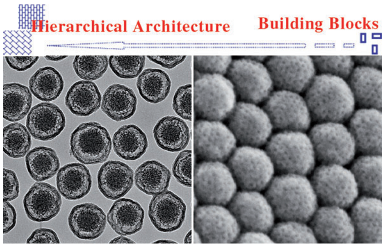
Detecting metal contamination in surface/ground water is crucial for protecting human health. The design and synthesis of metal-binding fluorescent nucleosides and development of a sensor array with DNA-polyfluorophores on beads is described, as well as their ability to detect and differentiate environmental contaminants in water.



Mesoporous Nanospheres

Y. Fang, G. Zheng, J. Yang, H. Tang,
Y. Zhang, B. Kong, Y. Lv, C. Xu, A. M. Asiri,
J. Zi, F. Zhang, D. Zhao* ___ **5366 – 5370**

Dual-Pore Mesoporous Carbon@Silica Composite Core–Shell Nanospheres for Multidrug Delivery

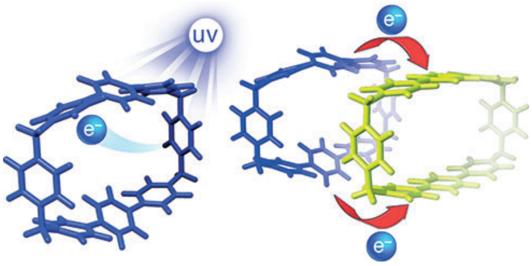


Novel nanocarriers benefit from their hierarchical mesostructure and dual-pore mesochannels, and the amphiphilicity of the hydrophobic carbon cores and hydrophilic silica shells. These composite nanospheres can be loaded with cisplatin and paclitaxel in multidrug combination therapy for the treatment of human ovarian cancer.

Electron Transfer

S. M. Dyar, J. C. Barnes, M. Juríček,
J. F. Stoddart, D. T. Co, R. M. Young,*
M. R. Wasielewski* ________ **5371 – 5375**

Electron Transfer and Multi-Electron Accumulation in ExBox^{4+}

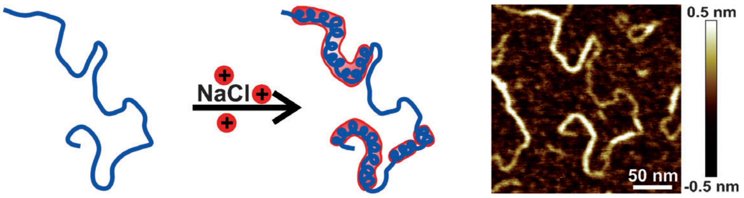


From outside the box: A viologen-based cyclophane ExBox^{4+} is photoexcited revealing a new through-bond pathway for electron transfer to ExBox^{4+}. The solid-state structure with both redox states ExBox^{4+} and ExBox^{2+} present, confirms that transferred electrons cause ExBox^{2+} to become flattened and form semiquinoidal structures capable of stabilizing unpaired electrons.

Coil–Helix Transition

L. Schefer, J. Adamcik,
R. Mezzenga* ______ 5376 – 5379

Unravelling Secondary Structure Changes on Individual Anionic Polysaccharide Chains by Atomic Force Microscopy

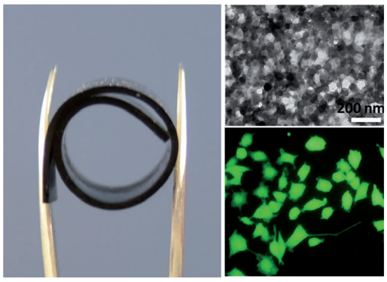


The coil–helix transition within single chains of anionic carrageenan polysaccharides is resolved in situ by atomic force microscopy, as a result of the presence of monovalent ions close to physiological conditions (see picture). Polymer statistical analysis demonstrates a modulation of the rigidity and topological features of individual polyelectrolyte chains upon this conformational change.

Nanocomposites

Z. Shi, H. Gao, J. Feng, B. Ding, X. Cao,*
S. Kuga, Y. Wang, L. Zhang,
J. Cai* ______ 5380 – 5384

In Situ Synthesis of Robust Conductive Cellulose/Polypyrrole Composite Aerogels and Their Potential Application in Nerve Regeneration

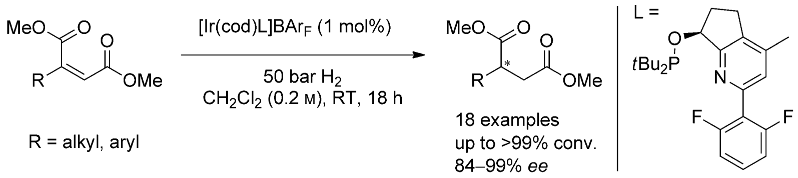


Composite gels prepared from nanoporous cellulose gel and in situ formed polypyrrole nanoparticles have low density, large surface area, high mechanical strength, sufficient electrical conductivity, no cytotoxicity, and neural differentiation ability. This robust conductive gel/aerogel will be useful for the development of materials for nerve regeneration, carbon capture, catalyst supports, and many other applications.

Asymmetric Catalysis

M. Bernasconi, M.-A. Müller,
A. Pfaltz* ______ 5385 – 5388

Asymmetric Hydrogenation of Maleic Acid Diesters and Anhydrides

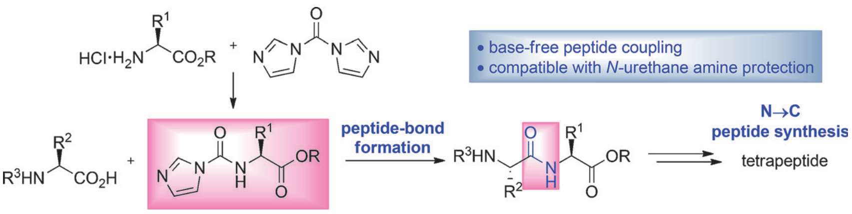


An attractive enantioselective route to 2-alkyl- and 2-aryl-substituted succinic acid derivatives is opened up by the asymmetric hydrogenation of maleic and fumaric acid derivatives, using the new catalyst [Ir(cod)**L**]$\mathrm{BAr_F}$, derived from a 2,6-difluorophenyl-substituted pyridine-phosphinite ligand. The products are valuable chiral building blocks having a structural motif found in many bioactive compounds. cod = 1,5-cyclooctadiene.

Peptide Synthesis

J.-S. Suppo, G. Subra, M. Bergès,
R. Marcia de Figueiredo,*
J.-M. Campagne* ______ 5389 – 5393

Inverse Peptide Synthesis via Activated α-Aminoesters

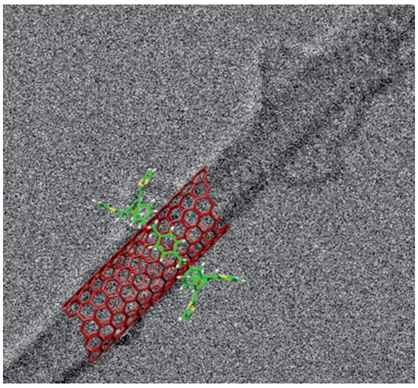


How to advance by going into reverse: In a mild and practical procedure for peptide-bond formation, free α-aminoesters were activated by treatment with N,N′-carbonyldiimidazole, instead of activating the carboxylic acid functionality (see scheme). The method provided a straightforward route to dipeptides, and its applicability to iterative peptide synthesis was illustrated by the synthesis of a tetrapeptide in the challenging reverse N→C direction.

Carbon Nanotubes

A. de Juan, Y. Pouillon, L. Ruiz-González, A. Torres-Pardo, S. Casado, N. Martín, Á. Rubio, E. M. Pérez* ____ **5394 – 5400**

Mechanically Interlocked Single-Wall Carbon Nanotubes

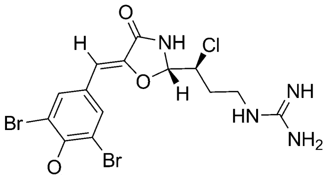


Nanotubes in MINT condition! In a clipping reaction, macrocycles were formed by ring-closing metathesis around single-wall nanotubes (SWNTs) as "threads" to produce rotaxane-type species: mechanically interlocked derivatives of carbon nanotubes (MINTs; see picture). Extensive characterization, including high-resolution STEM and control experiments, proved the interlocked nature of the products.

Natural Product Synthesis

N. V. Shymanska, I. H. An, J. G. Pierce* ____ **5401 – 5404**

A Rapid Synthesis of 4-Oxazolidinones: Total Synthesis of Synoxazolidinones A and B



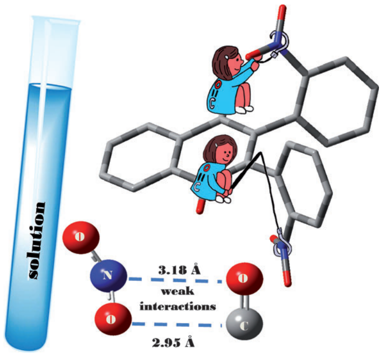
Synoxazolidinone A

Synthetic synoxazolidinones: A five-step total synthesis of the marine natural product synoxazolidinone A was achieved through a diastereoselective imine acylation/cyclization cascade. Synoxazolidinone B and a series of analogues were also prepared to explore the potential of these 4-oxazolidinones as antimicrobial agents. The results revealed simplified dichloro derivatives that are equally potent against several bacterial strains.

Weak Interactions

M. Chiarucci, A. Ciogli, M. Mancinelli, S. Ranieri, A. Mazzanti* ____ **5405 – 5409**

The Experimental Observation of the Intramolecular NO$_2$/CO Interaction in Solution

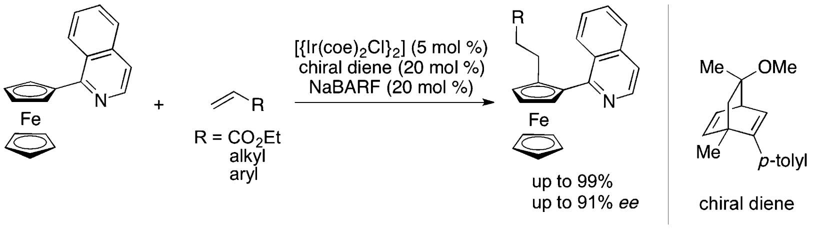


Might without muscle: The weak electrostatic interaction between nitro and carbonyl moieties has been observed by means of variable-temperature NMR spectroscopy. Its energetic contribution was evaluated to be about 3 kcal mol^{-1} by DFT calculations, and confirmed by the measurement of internal energy barriers to the rotation of suitable nitroaryl rings (see picture).

C–H Activation

T. Shibata,* T. Shizuno ____ **5410 – 5413**

Iridium-Catalyzed Enantioselective C–H Alkylation of Ferrocenes with Alkenes Using Chiral Diene Ligands

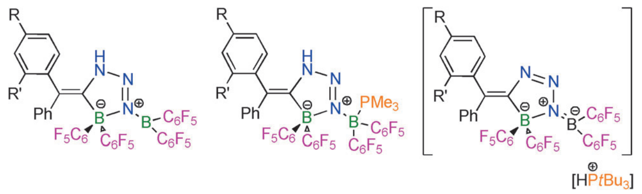


Director's cut: The first catalytic and enantioselective C–H alkylation of ferrocene derivatives with various alkenes was achieved. A cationic iridium complex, having a chiral diene ligand, and an isoquinolyl moiety as a directing group are essential for regioselective and enantioselective C–H bond activation. coe = cyclooctene, NaBARF = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

Cyclization

D. Winkelhaus,
D. W. Stephan* ______ 5414 – 5417

Boron Perturbed Click Reactions Prompt Aromatic C−H Activations

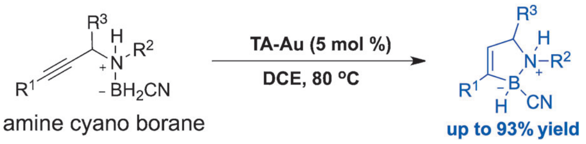


Click on B: The reaction of bis(pentafluorophenyl)boron alkynes and azides leads to unusual N_3BC heterocycles (see scheme) resulting from aromatic C−H activation of benzene and toluene. While subsequent treatment of the heterocycle with PMe_3 gave the P−B adduct, reaction with $PtBu_3$ effected deprotonation to generate the corresponding phosphonium salt.

Homogeneous Catalysis

Q. Wang, S. E. Motika, N. G. Akhmedov,
J. L. Petersen, X. Shi* ______ 5418 – 5422

Synthesis of Cyclic Amine Boranes through Triazole-Gold(I)-Catalyzed Alkyne Hydroboration

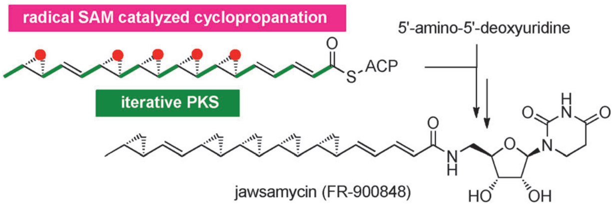


Stable and active: The first catalytic alkyne hydroboration of propargyl amine boranecarbonitrile is accomplished. While the typical [L-Au]$^+$ species decomposed within minutes upon addition of amine boranecarbonitriles, the triazole-modified gold catalysts (TA-Au) remained active and allowed formation of 1,2-BN-cyclopentenes in excellent yields.

Polyketide Biosynthesis

T. Hiratsuka, H. Suzuki, R. Kariya, T. Seo,
A. Minami, H. Oikawa* ______ 5423 – 5426

Biosynthesis of the Structurally Unique Polycyclopropanated Polyketide–Nucleoside Hybrid Jawsamycin (FR-900848)

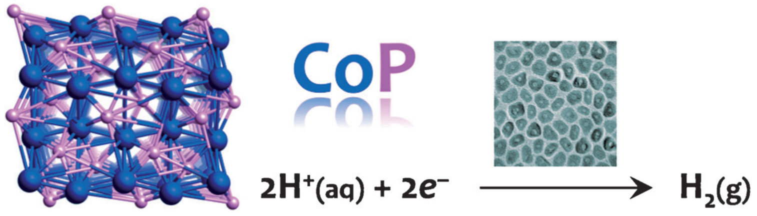


Jaws of life: The biosynthetic gene cluster of antifungal agent jawsamycin (FR-900848) has been identified by heterologous expression. A series of gene inactivations and in vitro and in vivo analysis of the key enzymes established their functions. A novel iterative polyketide synthase is proposed to collaborate with a trans-acting ketoreductase and a radical SAM cyclopropanase in constructing the unique polycyclopropanated backbone.

Hydrogen Evolution

E. J. Popczun, C. G. Read, C. W. Roske,
N. S. Lewis,* R. E. Schaak* ______ 5427 – 5430

Highly Active Electrocatalysis of the Hydrogen Evolution Reaction by Cobalt Phosphide Nanoparticles

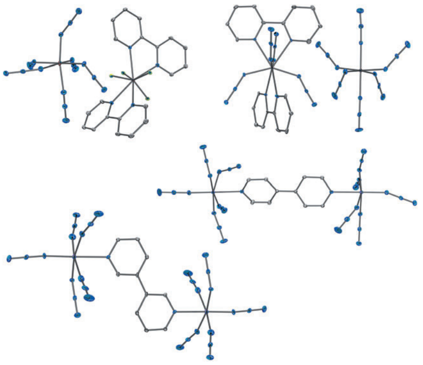


One step closer to Pt: Nanoparticles of cobalt phosphide (CoP) catalyze the hydrogen evolution reaction with high activity and stability under strongly acidic conditions. Its electrocatalytic performance places CoP amongst the best Earth-abundant alternatives to platinum.

Polyazides

R. Haiges,* P. Deokar,
K. O. Christe ______ 5431 – 5434

Coordination Adducts of Niobium(V) and Tantalum(V) Azide $M(N_3)_5$ (M = Nb, Ta) with Nitrogen Donor Ligands and their Self-Ionization

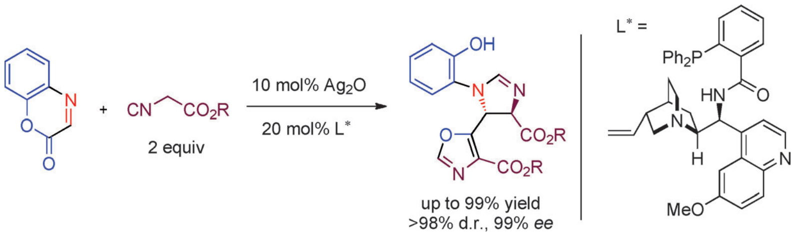


Several donor–acceptor adducts of niobium and tantalum pentaazide with N-donor ligands have been prepared from the pentafluorides by fluoride–azide exchange with Me_3SiN_3 in the presence of the corresponding donor ligand. With 2,2′-bipyridine and 1,10-phenanthroline, self-ionization products were formed, whereas 3,3′- and 4,4′-bipyridine gave neutral pentaazide adducts $(M(N_3)_5)_2{\cdot}L$ (see picture).

Asymmetric Catalysis

P.-L. Shao, J.-Y. Liao, Y. A. Ho,
Y. Zhao* ______ 5435 – 5439

Highly Diastereo- and Enantioselective Silver-Catalyzed Double [3+2] Cyclization of α-Imino Esters with Isocyanoacetate

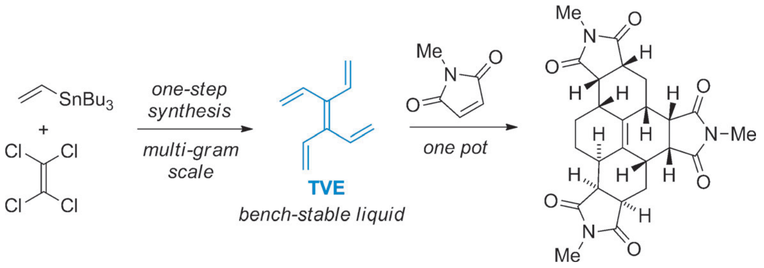


Double up: An unprecedented silver-catalyzed title reaction has been developed and provides access to directly linked oxazole-imidazolines. A highly diastereo- and enantioselective variant was also realized using the catalyst Ag/**L***. The products can be easily transformed into highly functionalized chiral α,β-diamino esters or imidazolinium salts which are useful motifs in asymmetric synthesis and catalysis.

Hydrocarbons

E. J. Lindeboom, A. C. Willis,*
M. N. Paddon-Row,*
M. S. Sherburn* ______ 5440 – 5443

Tetravinylethylene

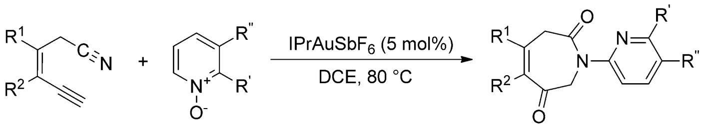


Targets very efficiently: The forgotten hydrocarbon, tetravinylethylene (TVE, scheme) is a bench-stable compound that can be synthesized in one step from commercially available starting materials. TVE is a vehicle for rapid complex molecule synthesis through one-pot sequences involving the stereoselective assembly of up to seven C–C bonds.

Homogeneous Catalysis

S. N. Karad, R.-S. Liu* ______ 5444 – 5448

Gold-Catalyzed 1,2-Oxoarylations of Nitriles with Pyridine-Derived Oxides

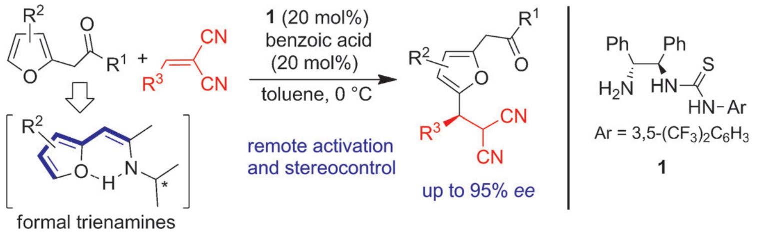


Spill the (car)benes: Reported herein is the first successful gold-catalyzed oxoarylation of nitriles with pyridine-derived *N*-oxides using gold carbenes as initiators (see scheme; DCE = 1,2-dichloroethane, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene). These oxoarylations were also achieved satisfactorily in intermolecular three-component oxidations using a variety of alkenyldiazo esters, nitriles, and pyridine-based *N*-oxides.

Organocatalysis

J.-L. Li, C.-Z. Yue, P.-Q. Chen, Y.-C. Xiao, Y.-C. Chen* ________ **5449 – 5452**

Remote Enantioselective Friedel–Crafts Alkylations of Furans through HOMO Activation



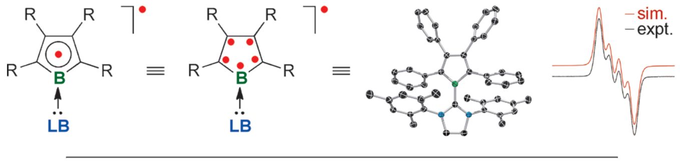
Alternative strategy: An asymmetric and regioselective Friedel–Crafts alkylation reaction of 2-furfuryl ketones and alkylidenemalononitriles was developed and involves the in situ generation of a formal HOMO-raised trienamine species. A diversity of alkylation products were produced in moderate to excellent enantioselectivity under the catalysis of a chiral bifunctional primary amine-thiourea (**1**).

Boron Radicals

R. Bertermann, H. Braunschweig,* R. D. Dewhurst, C. Hörl, T. Kramer, I. Krummenacher ________ **5453 – 5457**

Evidence for Extensive Single-Electron-Transfer Chemistry in Boryl Anions: Isolation and Reactivity of a Neutral Borole Radical

Inside Back Cover



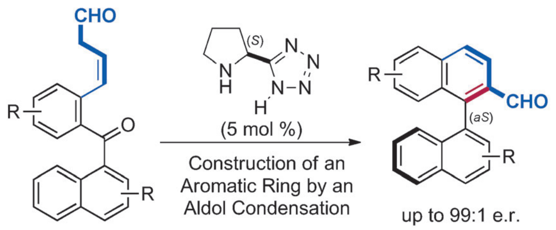
Neutral borolyl radical: *charge: 0, π electrons: 5, unpaired electrons: 1*

ReSETting perspectives: A borolyl anion displays single-electron-transfer (SET) processes in its reaction with triorganotetrel halides. This was confirmed by the isolation of the first neutral borolyl radical. This radical reactivity was exploited in the synthesis of compounds with rare B–Sn and B–Pb bonds, the latter of which is the first structurally characterized species with a "noncluster" B–Pb bond.

Synthetic Methods

A. Link, C. Sparr* ________ **5458 – 5461**

Organocatalytic Atroposelective Aldol Condensation: Synthesis of Axially Chiral Biaryls by Arene Formation

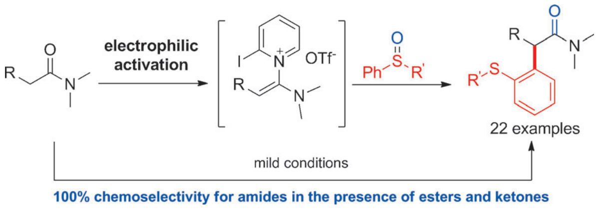


Head-turning! An organocatalytic atroposelective aldol condensation to tri-*ortho*-substituted biaryls is described. Key to the process is an efficient transfer of the stereochemical information of a secondary amine catalyst into the axis of chirality of binaphthyl products. The reaction proceeds analogous to the aromatic polyketide biosynthesis and is distinct in its initiation by virtue of dienamine formation. This method allows for the synthesis of axially chiral biaryls with remarkable atroposelectivity of up to e.r. 99:1.

Amide Activation

B. Peng, D. Geerdink, C. Farès, N. Maulide* ———— **5462 – 5466**

Chemoselective Intermolecular α-Arylation of Amides



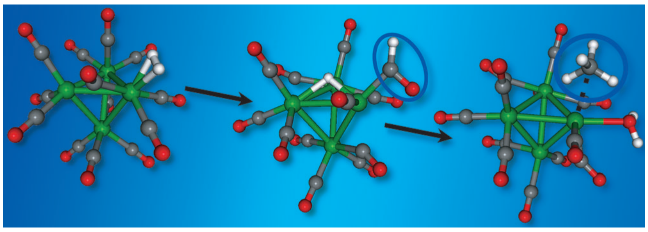
Arylating me softly: A new approach for the fully chemoselective α-arylation of amides has been developed. When electrophilic amide activation is employed, aryl groups can be regioselectively introduced in the position α to the amide, and that even in the presence of esters or alkyl ketones. Mechanistic studies emphasize a remarkably subtle base effect in this transformation.

CO Methanation

S. M. Lang, T. M. Bernhardt,* M. Krstić, V. Bonačić-Koutecký* ———— **5467 – 5471**

The Origin of the Selectivity and Activity of Ruthenium-Cluster Catalysts for Fuel-Cell Feed-Gas Purification: A Gas-Phase Approach

Inside Cover



Be selective! Efficient CO methanation catalysts for fuel-cell feed-gas purification have to selectively convert CO while leaving CO_2 untouched. Employing free clusters as model systems, mechanistic insights are obtained that provide the basis for understanding and improving the performance of supported ruthenium catalysts in this reaction (see picture: Ru green, C gray, H white, O red).

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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Angewandte Corrigendum

Metal–Organic Organopolymeric Hybrid Framework by Reversible [2+2] Cycloaddition Reaction

I.-H. Park, A. Chanthapally, Z. Zhang, S. S. Lee,* M. J. Zaworotko,* J. J. Vittal* ———— **414–419**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201308606

In this Communication, the topology of the network was given incorrectly in pages 417 and 418: **jjv1** should be replaced by *jjv*1. Further, an important citation for this topological analysis was missed. Hence the third sentence in the second paragraph on page 417 is rewritten as follows:

"It is this infinite extension of the ligand which results in a new (4,4)-connected net, which was analyzed using TOPOS[13b–d] and was named as *jjv*1 (Figure 5), with point symbol $\{6.8^5\}\{6^4.8^2\}$ and vertex symbol $[6_2.8_2.8_5.8_5.8_5.8_5]$ $[6.6.6.6.8_2.10_{12}]$."

In addition, reference [13] needs to be changed as shown below.

The authors would like to acknowledge Prof. Davide M. Proserpio for help with the suggestions on the new topology as well as for correcting the representation error.

---

[13] a) A. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7; b) V. A. Blatov, *TOPOS 4.0 Professional*, Commission on Crystallographic Computing, IUCr, **2006**; c) E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov, D. M. Proserpio, *CrystEngComm* **2011**, *13*, 3947; d) V. A. Blatov, *Struct. Chem.* **2012**, *23*, 955.

Angewandte Addendum

It was called to the attention of the correspondence authors of this communication that the statement “Adducts of an electronegative central anion, such as Cl^-, with halogen molecules, such as I_2, attached, are not known.” should not be maintained. Indeed, $[Cl(I_2)_4]^-$ contains the linear anion $[Cl(I_2)]^-$ which has been observed apparently for the first time in the crystal structure of $(Phen)_2[[Cl_2I][ClI_2]$.[1] The isolated anion $[Cl(I_2)_4]^-$ may also be cut out of the anionic network in the crystal structure of $[(Ph)_3PCl]_2[Cl_2I_{14}]$.[2] However, the “anion” $[Cl_2I_{14}]^{2-} \rightarrow [ClI_7]^-$, better written as $[\{Cl(I_2)_{4/2}(I_2)\}(I_2)_{1/2}]^-$, contains the tetragonal pyramid $\{Cl(I_2)_{4/2}(I_2)\}$, whose not exactly planar base $Cl(I_2)_4$ is connected with further $[Cl(I_2)_4]$ units. Synthesis and crystal structure of $[(H_5O_2)12b15c5)_2][Cl(I_2)_4]$ are, by the way, taken from Ref. [3].

---

[1] Y.-Q. Wang, Z.-M. Wang, C.-S. Liao, C.-H. Yan, *Acta Cryst.* **1999**, *C55*, 1503–1506.
[2] M. Wolff, A. Okrut, C. Feldmann, *Inorg. Chem.* **2011**, *50*, 11683–11694.
[3] C. Walbaum, *Neue Poly(inter)halogenide mit Kronenether-stabilisierten Kationen*, Dissertation, Universität zu Köln, **2009**; publicly available from http://kups.ub.uni-koeln.de/id/eprint/2952.

Iodine–Iodine Bonding makes Tetra(diiodine)chloride, $[Cl(I_2)_4]^-$, Planar

C. Walbaum, M. Richter, U. Sachs, I. Pantenburg, S. Riedel,* A.-V. Mudring,* G. Meyer* **12732–12735**

Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201305412

Angewandte Corrigendum

The authors wish to rectify the reported concentrations of metals in MWCNTs and GONRs used in the study. The concentrations of metals obtained from ICP-MS data reported in the original Communication were presented as obtained directly from the equipment without taking into account the dilution factor introduced during the microwave digestion procedure. This error in no way affects the conclusions of the paper. The following changes should be applied to the article text to reflect the true concentrations of the metals in the carbon materials:

page 8685, column 1:
“parts-per-billion” change to “parts-per-million”

page 8686, column 2:
“1130.9 ppb to 28.6 ppb” change to “5463.3 ppm to 193.2 ppm”
“20.7 ppb to 1.9 ppb” change to “100.2 ppm to 13.0 ppm”
“78.6 ppb to 46.5 ppb” change to “379.5 ppm to 314.0 ppm”

page 8687, column 1:
“ppb” change to “ppm”
“less than 2 ppb” change to “13 ppm”

page 8687, column 2:
“ppb” change to “ppm”

Graphene Oxide Nanoribbons from the Oxidative Opening of Carbon Nanotubes Retain Electrochemically Active Metallic Impurities

C. H. A. Wong, C. K. Chua, B. Khezri, R. D. Webster, M. Pumera* **8685–8688**

Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201303837