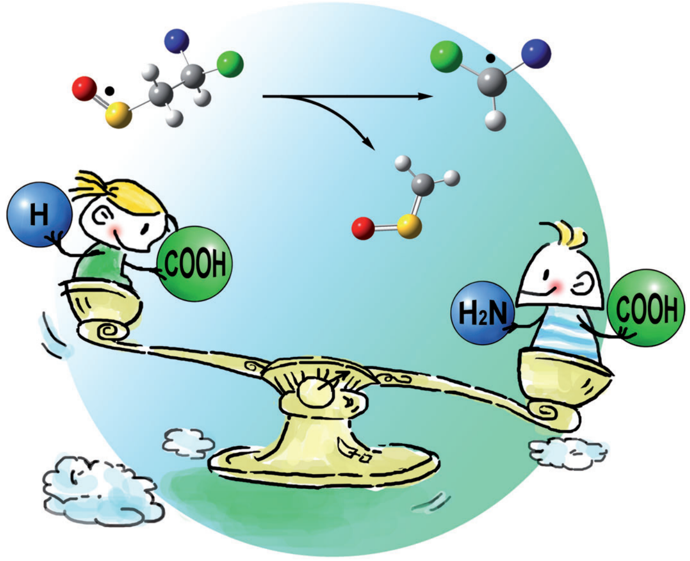
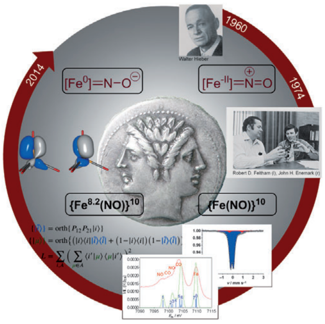
Radical stability …

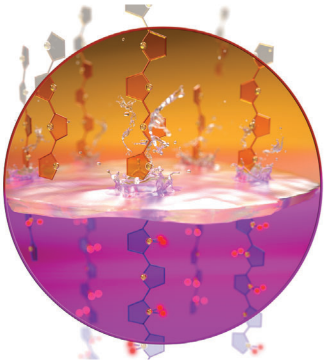


… can be assessed by a new mass spectrometric approach proposed by L. Tan and co-workers in their Communication on page 1887 ff. The stability of carbon-centered bioorganic radicals is evaluated by a method based on the gas-phase dissociation of sulfinyl radical ions. The degree of CH_2SO loss is found to be correlated with the stability of the as-formed radical species, which can be molecularly tuned by the electronic effect of the neighboring groups.

$[Fe(CO)_3(NO)]^-$

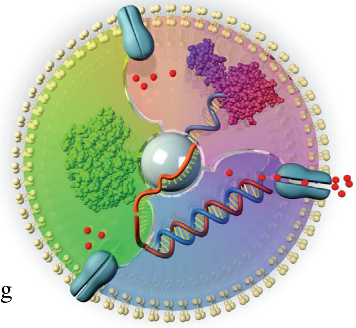
In their Communication on page 1790 ff., B. Plietker and co-workers show by spectroscopic and theoretical investigations that $[Fe(CO)_3(NO)]^-$ as well as not being an Fe^{-II} species, also does not contain an Fe–N σ bond.





Polymer Chemistry

The selective oxidation of thiophene-containing polymers with $HOF\cdot CH_3CN$ to give products with modified electronic properties is described by L. M. Campos et al. in their Communication on page 1832 ff.



Biomimetics

X. Chen, M. Yang et al. demonstrate in their Communication on page 1997 ff. synthetic RISC-mimic nanocomplexes for sequence-specific gene silencing, which are designed to target multidrug resistance.

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Editorial

"… Which is the most stable molecular structure of the sum formula $C_6H_{12}O_6$? Nobody really knows yet, but for sure it is not glucose … The winners—and there is just one for every reasonable sum formula—might be termed 'Guinness molecules' …"
Read more in the Editorial by Martin Suhm.

Service

Author Profile

"The worst advice I have ever been given was not to study chemistry.
My favorite song is any song by Fairuz …"
This and more about Ashraf Brik can be found on page 1738.

News

S. R. Waldvogel

F. Neese

G. Centi

Books

More Dead Ends and Detours

Miguel A. Sierra, Maria C. de la Torre, Fernando P. Cossío

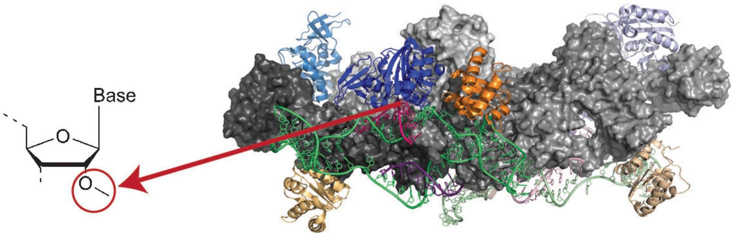
reviewed by S. McKerrall, P. Baran **1740**

Highlights

RNA Modification

M. Hengesbach, H. Schwalbe* **1742 – 1744**

Structural Basis for Regulation of Ribosomal RNA 2′-O-Methylation



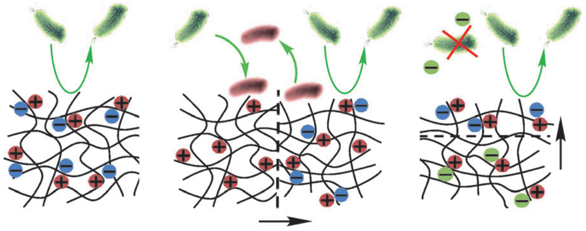
Methods that interrogate different, yet overlapping structural-size ranges were integrated to gain high-resolution information on the *Pyrococcus furiosus* box C/D ribonucleoprotein complex. The new structure shows how 2′-O-methylation of RNA substrates through four active methyltransferases occurs in a strictly sequential manner.

Minireviews

Functional Materials

L. Mi, S. Jiang* **1746 – 1754**

Integrated Antimicrobial and Nonfouling Zwitterionic Polymers



Fighting germs: Molecular design leads to zwitterionic nonfouling polymers with surface bactericidal and bulk antimicrobial functionalities (sketched in the picture). This functional versatility makes zwitterionic polymers a promising alternative and improvement to the conventional poly(ethylene glycol) (PEG) nonfouling materials.

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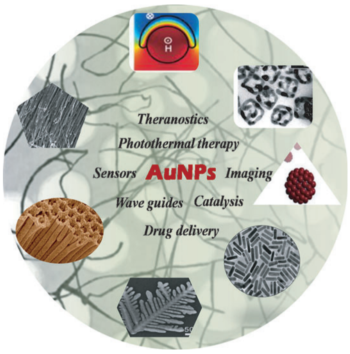
Reviews

Nanoparticles

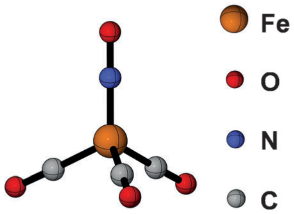


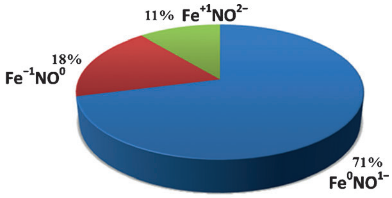
Function follows form: Anisotropic gold nanoparticles (AuNPs) have attracted the interest of scientists for over a century. Research in this field has considerably accelerated since 2000 with the synthesis of numerous 1D, 2D, and 3D shapes as well as hollow AuNP structures. The synthetic modes, variety of shapes, applications, and toxicity issues of this fast-growing class of nanomaterials are reviewed here.

Communications

Iron Catalysis

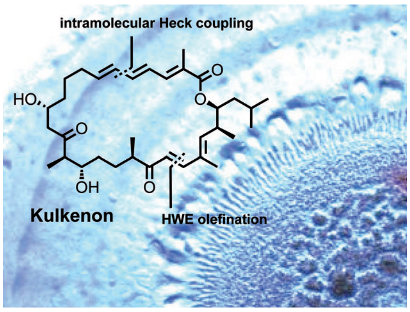
Frontispiece





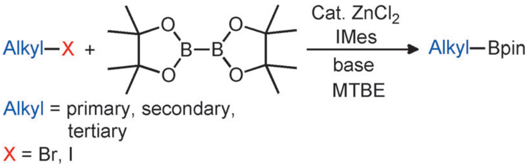
Even more complex: Spectroscopic and quantum chemical investigations show that the complex ferrate $[\text{Fe(CO)}_3\text{(NO)}]^-$ cannot be considered to be a Fe^{-II} species, but rather is predominantly an Fe^0 species, in which the metal is covalent bound to NO^- by two π bonds. A metal–N σ bond is not observed.

Natural Products



Similar but not identical: The related natural products sulfangolid and kulkenon exhibit different configurations, which only became apparent by synthesizing the proposed structure and comparison with the authentic data. A combination of NOE experiments and computational conformational search identified the correct structure of kulkenon.

Zinc-Catalyzed Borylation



Coupling a la carte: A catalytic system based on a Zn^{II} N-heterocyclic carbene precursor has been developed for the cross-coupling reaction of alkyl halides with diboron reagents (see scheme). This is a novel use of a Group 12 catalyst for C–X borylation. IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

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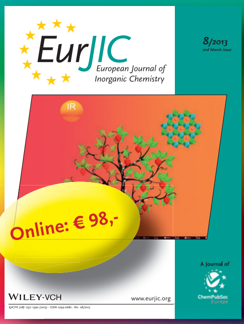
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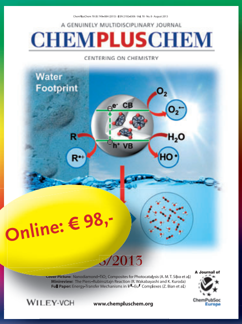
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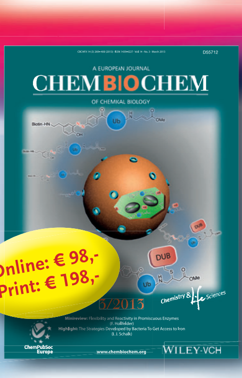
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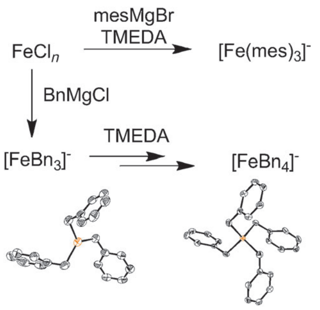
Homoleptic Iron Complexes

R. B. Bedford,* P. B. Brenner, E. Carter,
P. M. Cogswell, M. F. Haddow,
J. N. Harvey, D. M. Murphy, J. Nunn,
C. H. Woodall — **1804–1808**

TMEDA in Iron-Catalyzed Kumada Coupling: Amine Adduct versus Homoleptic "ate" Complex Formation

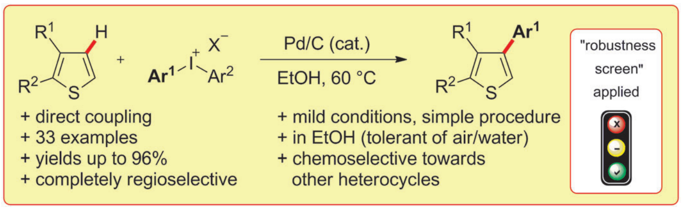
Casting iron in catalytic roles: Chelating diamine ligands such as TMEDA are routinely used in iron-catalyzed cross-coupling reactions of aryl Grignard reagents. However, it was found that under catalytically relevant conditions, there is little evidence for their coordination to iron centers; homoleptic anionic organoiron species are produced instead.



C–H Functionalization

D.-T. D. Tang, K. D. Collins, J. B. Ernst,
F. Glorius* — **1809–1813**

Pd/C as a Catalyst for Completely Regioselective C–H Functionalization of Thiophenes under Mild Conditions

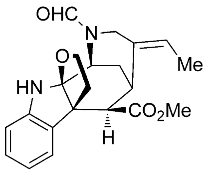


I$^+$ can do better! Pd/C can be used without ligands or additives to catalyze the completely C3-selective arylation of diversely substituted thiophenes and benzo[*b*]thiophenes under mild reaction conditions. The physical nature of the catalytic species was investigated and the mechanism was studied. Relative rate data generated in a "robustness screen" were used to design a complex substrate that undergoes highly chemoselective sequential functionalization.

Natural Products Synthesis

M. Teng, W. Zi, D. Ma* — **1814–1817**

Total Synthesis of the Monoterpenoid Indole Alkaloid (±)-Aspidophylline A



aspidophylline A

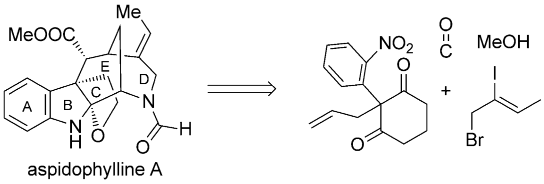
Nice and concise: In a 15-step total synthesis of (±)-aspidophylline A (see structure), an intramolecular oxidative coupling was used to create the tetracyclic furoindoline motif, and a [Ni(cod)$_2$]-mediated cyclization was used to install the bridging piperidine ring. The simultaneous installation of two rings of the pentacyclic natural product by oxidative coupling was key to the efficiency of the synthesis.

Natural Products Synthesis

W. Ren, Q. Wang, J. Zhu* — **1818–1821**

Total Synthesis of (±)-Aspidophylline A

Inside Cover

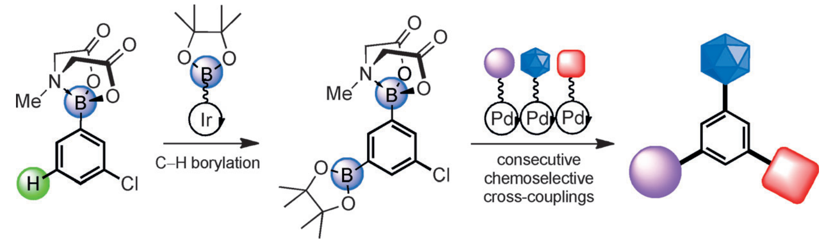


Simplicity in complexity: In an efficient total synthesis of aspidophylline A, rapid access was gained to a fully functionalized dihydrocarbazole by the desymmetrization of a 2,2-disubstituted cyclohexane-1,3-dione (see scheme). A further key step was the intramolecular azidoalkoxylation of an enecarbamate to construct the fused furoindoline system and install an azido group. The final ring was formed by an intramolecular Michael addition.

Chemoselective Coupling

L. Xu, S. Ding, P. Li* ______ **1822 – 1826**

Site-Differentiated Polyboron Arenes Prepared by Direct C–H Borylation and Their Highly Selective Suzuki–Miyaura Cross-Coupling Reactions

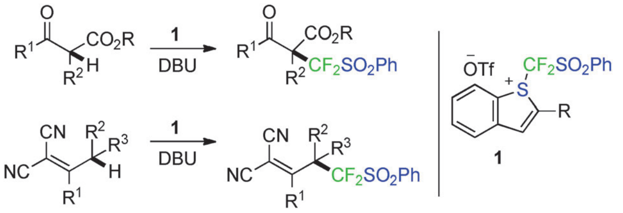


Assembly line: The title reaction was developed for the synthesis of differentiated di- and polyboron-substituted (hetero)arenes from readily available (hetero)aryl *N*-methyliminodiacetic acid boronates. Subsequent chemoselective and consecutive Suzuki–Miyaura cross-coupling reactions allowed rapid, efficient, and flexible synthesis of multifunctionalized poly(hetero)arenes from simple building blocks.

Synthetic Methods

X. Wang, G. Liu, X.-H. Xu, N. Shibata, E. Tokunaga, N. Shibata* __ **1827 – 1831**

S-((Phenylsulfonyl)difluoromethyl)-thiophenium Salts: Carbon-Selective Electrophilic Difluoromethylation of β-Ketoesters, β-Diketones, and Dicyanoalkylidenes



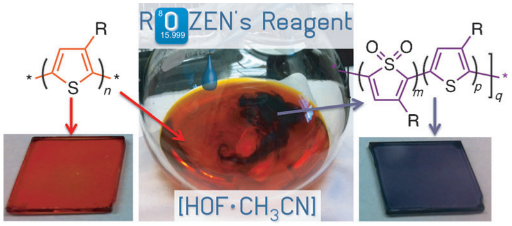
S and F join forces: The title salts were designed and prepared by a triflic acid catalyzed intramolecular cyclization of *ortho*-ethynyl aryldifluoromethyl sulfanes. The salts **1** were efficient as electrophilic difluoromethylating reagents for introducing a CF_2H group to sp^3-hybridized carbon nucleophiles. Enantioselective electrophilic difluoromethylation was also investigated. DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene, Tf = trifluoromethanesulfonyl.

Polymer Chemistry

S. Wei, J. Xia, E. J. Dell, Y. Jiang, R. Song, H. Lee, P. Rodenbough, A. L. Briseno, L. M. Campos* ______ **1832 – 1836**

Bandgap Engineering through Controlled Oxidation of Polythiophenes

Inside Back Cover

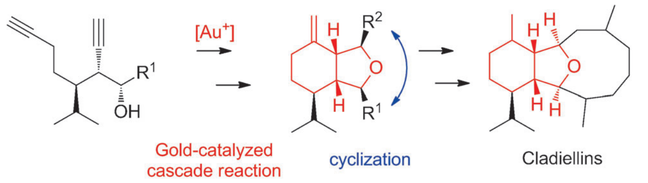


Rusted root: Rozen's reagent ($HOF \cdot CH_3CN$) can convert polythiophenes to polythiophene-1,1-dioxides. The oxidation of thiophene-containing polymers, including telechelic polythiophenes, can be controlled with this potent, yet orthogonal reagent under mild conditions. By modulating the backbone of well-defined polymers, rather than varying the monomers, this approach provides an efficient means to tune their electronic properties.

Natural Product Synthesis

G. Yue, Y. Zhang, L. Fang, C.-c. Li, T. Luo,*
Z. Yang* ______ **1837 – 1840**

Collective Synthesis of Cladiellins Based on the Gold-Catalyzed Cascade Reaction of 1,7-Diynes

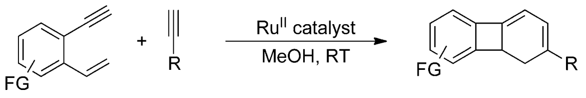


Clad(iellins) in gold: A gold-catalyzed tandem reaction of 1,7-diynes was previously developed to construct the 6-5-bicyclic ring systems that are present in a number of natural products. This reaction was applied to realize the total synthesis of nine members of the cladiellin family. This modular and efficient approach, which is enantio- and stereoselective, could also be used for the construction of other cladiellins and their analogues.

Biphenylenes

S. García-Rubín, C. González-Rodríguez,
C. García-Yebra, J. A. Varela,
M. A. Esteruelas,* C. Saá* _ **1841 – 1844**

Dihydrobiphenylenes through Ruthenium-Catalyzed [2+2+2] Cycloadditions of *ortho*-Alkenylarylacetylenes with Alkynes

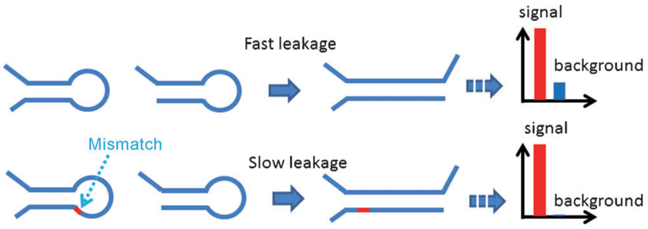


A new synthetic route to dihydrobiphenylenes involves a mild Ru^{II}-catalyzed [2+2+2] dimerization of *ortho*-alkenylarylacetylenes or its more versatile variant, the Ru-catalyzed [2+2+2] cycloaddition of *ortho*-ethynylstyrenes with alkynes. The mechanistic aspects of this [2+2+2] cycloaddition are also discussed.

Bioanalysis

Y. Jiang, S. Bhadra, B. Li,
A. D. Ellington* ______ **1845 – 1848**

Mismatches Improve the Performance of Strand-Displacement Nucleic Acid Circuits



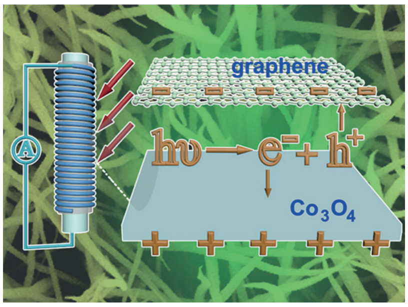
Catalytic hairpin assembly (CHA) is a useful amplification method for the detection of nucleic acids. CHA circuits, however, have been shown to execute nonspecifically even in the absence of catalyst, which can make quantitation of lower input concentrations difficult. By introducing two mismatched bases into a specific domain on the circuit, the signal-to-background ratio can be improved from less than 10:1 to over 100:1.

Integrated Devices

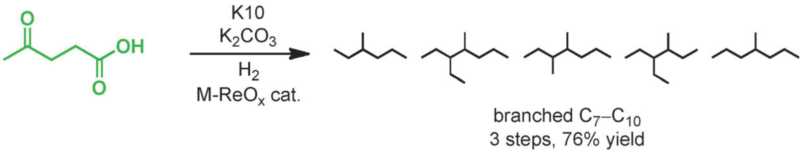
X. F. Wang, B. Liu, R. Liu, Q. F. Wang,
X. J. Hou, D. Chen,* R. M. Wang,*
G. Z. Shen* ______ **1849 – 1853**

Fiber-Based Flexible All-Solid-State Asymmetric Supercapacitors for Integrated Photodetecting System

All on a single fiber: Fiber-shaped all-solid-state asymmetric supercapacitors were prepared on Ni or Ti fibers. Furthermore, the combination of a supercapacitor and a photodetector based on graphene on carbon fibers as light-sensitive material gave a flexible integrated system on a single fiber to simultaneously realize energy storage and photodetection.

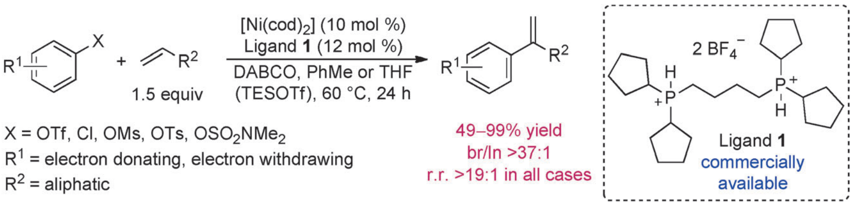


Renewable Chemicals



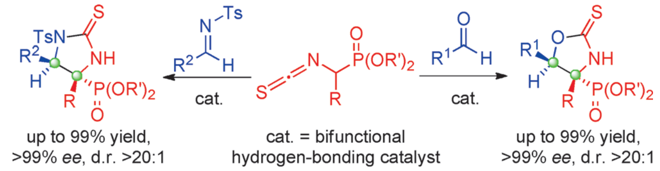
Fuel for thought: Biomass-derived levulinic acid can be converted in three simple steps via the angelica lactone dimer into branched, gasoline-range hydrocarbons in high yield by using a combination of oxophilic metal and noble metal catalysts (see scheme).

Mizoroki–Heck Chemistry



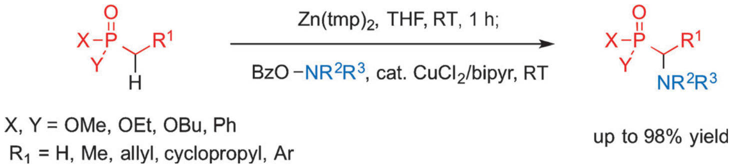
Branching out: A Ni-catalyzed Heck reaction for the preparation of 1,1-disubstituted alkenes is presented. High selectivity for the branched products is achieved with electronically unbiased aliphatic terminal olefins. Regioselectivities remain consistently high (≥19:1) throughout. TESOTf = triethylsilyl trifluoromethanesulfonate.

Asymmetric Synthesis



Correct chirality critical: Organocatalytic asymmetric Adol-type and Mannich-type reactions of α-isothiocyanato phosphonate have been realized. Michael addition was also applicable under the same catalytic conditions. This versatile approach provides a new route for the synthesis of diverse highly optically active functionalized α-amino phosphonic acid derivatives.

Synthetic Methods

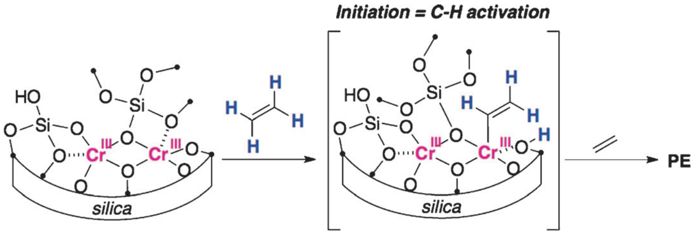


A direct approach to important α-amino phosphonic acids and derivatives, by using copper-catalyzed electrophilic amination of α-phosphonate zincates using O-acylhydroxylamines, is described. This amination is the first example of C–N bond formation which directly introduces acyclic and cyclic amines to the α-position of phosphonates in one step. The reaction proceeds at room temperature with as little as 0.5 mol% of the catalyst.

Polymerization Mechanisms

M. P. Conley, M. F. Delley, G. Siddiqi, G. Lapadula, S. Norsic, V. Monteil, O. V. Safonova, C. Copéret* **1872–1876**

Polymerization of Ethylene by Silica-Supported Dinuclear Cr^{III} Sites through an Initiation Step Involving C–H Bond Activation

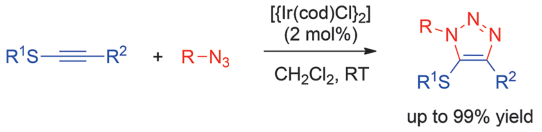


Three is better than two: Cr^{III} silicates, in contrast to the Cr^{II} analogues, were found to be efficient ethylene-polymerization catalysts that initiate the reaction without a cocatalyst through the heterolytic splitting of an ethylene C–H bond across a Cr–O bond (see picture). This study provides clues about the active sites and initiation mechanism of the industrial Phillips catalyst.

Click Chemistry

S. Ding, G. Jia,* J. Sun* **1877–1880**

Iridium-Catalyzed Intermolecular Azide–Alkyne Cycloaddition of Internal Thioalkynes under Mild Conditions

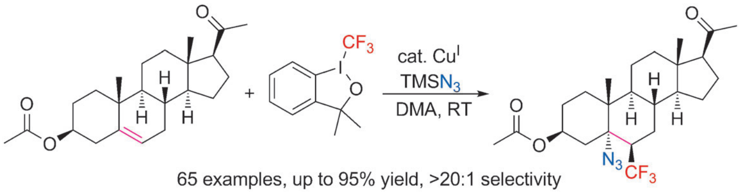


Sometimes it just clicks: An iridium-catalyzed azide–alkyne cycloaddition reaction (IrAAC) of electron-rich internal alkynes is described. This reaction represents the first efficient intermolecular AAC of thioalkynes. It exhibits remarkable features, such as high efficiency and regioselectivity, mild reaction conditions, easy operation, and excellent compatibility with air and a broad spectrum of organic and aqueous solvents.

Synthetic Methods

F. Wang, X. Qi, Z. Liang, P. Chen, G. Liu* **1881–1886**

Copper-Catalyzed Intermolecular Trifluoromethylazidation of Alkenes: Convenient Access to CF_3-Containing Alkyl Azides

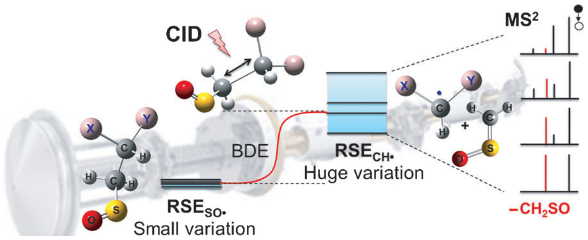


The title reaction proceeds with a CF_3^+ reagent under mild reaction conditions. This transformation presents a broad substrate scope and good functional-group tolerance. A variety of CF_3-containing organoazides are directly synthesized from a wide range of olefins, including activated and unactivated alkenes. The resulting products are easily transformed into the corresponding amine derivatives.

Radicals

L. Tan, H. Hu, J. S. Francisco,* Y. Xia* **1887–1890**

A Mass Spectrometric Approach for Probing the Stability of Bioorganic Radicals



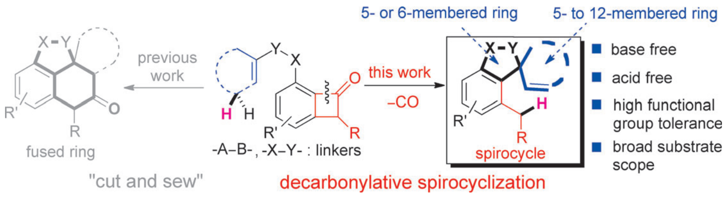
The dissociation of sulfinyl radical ions in the gas phase leads to a mass spectrometric approach to probe the stability of glycyl radical. CID = collision-induced dissociation, BDE = bond dissociation energy, RSE = radical stabilization energy.

Front Cover

C–C Activation

T. Xu, N. A. Savage,
G. Dong* ________________ 1891 – 1895

Rhodium(I)-Catalyzed Decarbonylative Spirocyclization through C–C Bond Cleavage of Benzocyclobutenones: An Efficient Approach to Functionalized Spirocycles

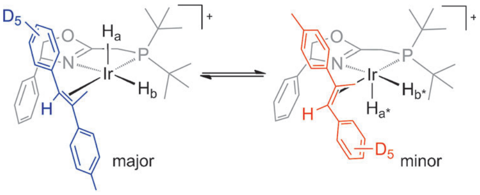


All-carbon spirocenters were formed by a decarbonylative coupling of trisubstituted cyclic olefins and benzocyclobutenones through C–C activation. The metal–ligand combination of $[\{Rh(CO)_2Cl\}_2]$ and $P(C_6F_5)_3$ catalyzed this transformation most efficiently; a range of spirocyclic rings was thus synthesized in good to excellent yields.

Reactive Intermediates

S. Gruber, A. Pfaltz* ________ 1896 – 1900

Asymmetric Hydrogenation with Iridium C,N and N,P Ligand Complexes: Characterization of Dihydride Intermediates with a Coordinated Alkene

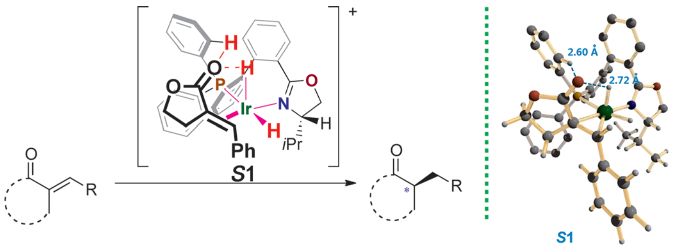


Previously elusive iridium dihydride alkene complexes (see scheme) have been identified and characterized by NMR spectroscopy in solution. Reactivity studies indicated that these complexes are catalytically competent intermediates. Additional H_2 is required to convert the catalyst-bound alkene into the hydrogenation product, supporting an Ir^{III}/Ir^{V} cycle via an $[Ir^{III}(H)_2(alkene)(H_2)(L)]^+$ intermediate.

Structure Elucidation

Y. Liu, I. D. Gridnev,*
W. Zhang* ________________ 1901 – 1905

Mechanism of the Asymmetric Hydrogenation of Exocyclic α,β-Unsaturated Carbonyl Compounds with an Iridium/BiphPhox Catalyst: NMR and DFT Studies

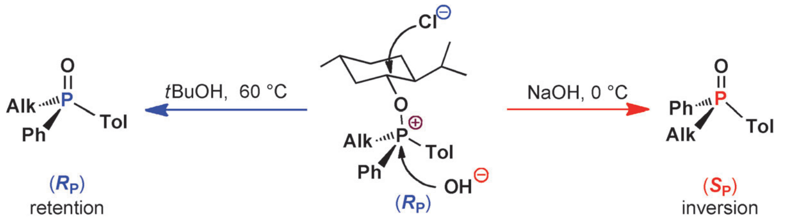


H in a fix: The title studies show an equilibrium of dinuclear iridium hydrides at low temperature after hydrogenation of the precatalyst. Computations of the conceivable *R* and *S* pathways allowed elucidation of the mechanism for enantioselection, thus affording computed optical yields which are consistent with the experimental values. The structure *S*1 features hydrogen bonding between the catalyst and the carbonyl group of the substrate.

Asymmetric Synthesis

K. Nikitin,* K. V. Rajendran,
H. Müller-Bunz,
D. G. Gilheany* 1906 – 1909

Turning Regioselectivity into Stereoselectivity: Efficient Dual Resolution of P-Stereogenic Phosphine Oxides through Bifurcation of the Reaction Pathway of a Common Intermediate

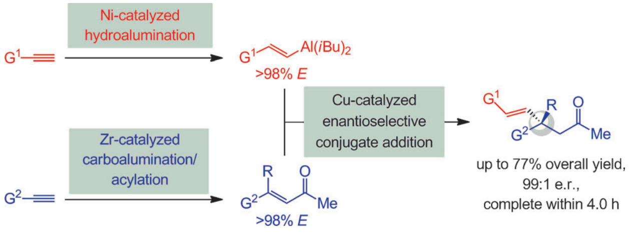


Railroad switch: Both enantiomers of *n*-alkylphenyl-*o*-tolylphosphine oxide have been prepared from a single intermediate, which functions as a stereochemical railroad switch. Arbuzov-type collapse of the (R_P)-alkoxyphosphonium chloride proceeds through C–O bond fission with retention of configuration at the phosphorus center, whereas alkaline hydrolysis leads to the S_P enantiomer through P–O bond cleavage.

Multicomponent Catalysis

K. P. McGrath,
A. H. Hoveyda* 1910 – 1914

A Multicomponent Ni-, Zr-, and Cu-Catalyzed Strategy for Enantioselective Synthesis of Alkenyl-Substituted Quaternary Carbons

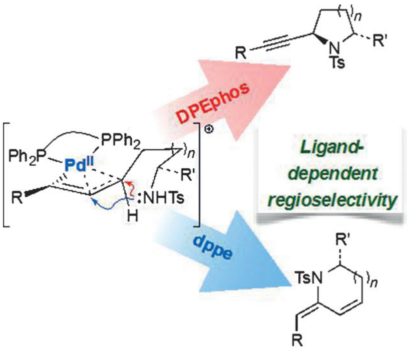


One-two-three punch: Ni-catalyzed alkyne hydroalumination, Zr-catalyzed alkyne carbometalation/acylation, and Cu-catalyzed enantioselective conjugate addition are combined for accessing acyclic organic molecules that contain an alkene-substituted quaternary carbon stereogenic center. The entire process takes less than four hours and affords products in up to 77% overall yield and 99:1 enantiomeric ratio.

Nitrogen Heterocycles

D. S. B. Daniels, A. S. Jones,
A. L. Thompson, R. S. Paton,*
E. A. Anderson* 1915 – 1920

Ligand Bite Angle-Dependent Palladium-Catalyzed Cyclization of Propargylic Carbonates to 2-Alkynyl Azacycles or Cyclic Dienamides

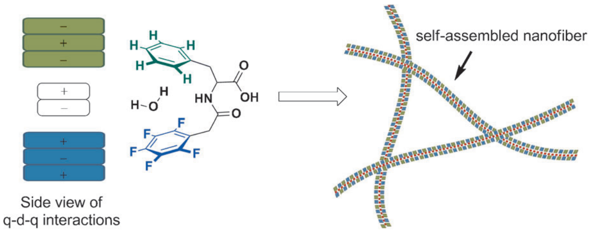


Chomp! The bite angle of bidentate phosphine ligands determined the course of the palladium-catalyzed cyclization of propargylic carbonates with sulfonamide nucleophiles. A small bite angle favored attack on the central C atom of the allenylpalladium intermediate, whereas alkynyl azacycles were formed from attack on the terminal C atom using ligands with a large bite angle.

Noncovalent Interactions

S.-M. Hsu, Y.-C. Lin, J.-W. Chang, Y.-H. Liu,
H.-C. Lin* **1921 – 1927**

Intramolecular Interactions of a Phenyl/Perfluorophenyl Pair in the Formation of Supramolecular Nanofibers and Hydrogels

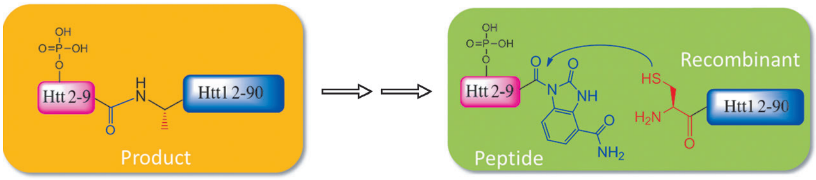


Intramolecular binding: The incorporation of a phenyl/perfluorophenyl pair into the structure of a peptide hydrogelator leads to the formation of the supramolecular nanofibers. The quadrupole–dipole–quadrupole (q-d-q) interactions between the aromatic rings facilitate self-assembly. This work illustrates the importance of the structure–hydrogelation relationship and provides new insights into the design of self-assembled nanobiomaterials.

Protein Modification

A. Ansaloni, Z. M. Wang, J. S. Jeong,
F. S. Ruggeri, G. Dietler,
H. A. Lashuel* **1928 – 1933**

One-Pot Semisynthesis of Exon 1 of the Huntingtin Protein: New Tools for Elucidating the Role of Posttranslational Modifications in the Pathogenesis of Huntington's Disease



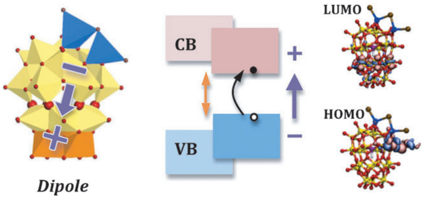
Tailor-made: A one-pot semisynthetic strategy that enables the site-specific introduction of posttranslational modifications within the N terminus of exon 1 of the Huntingtin protein (Httex1) is reported. This approach was applied to generate untagged wild-type and T3-phosphorylated Httex1. Httex1 with polyQ repeats below the pathogenic threshold (Httex1-23Q) was shown to aggregate in vitro and phosphorylation at T3 slows aggregation.

Polyoxotitanium Cages

Y. Lv, J. Cheng,* A. Steiner, L. Gan,
D. S. Wright* **1934 – 1938**

Dipole-Induced Band-Gap Reduction in an Inorganic Cage

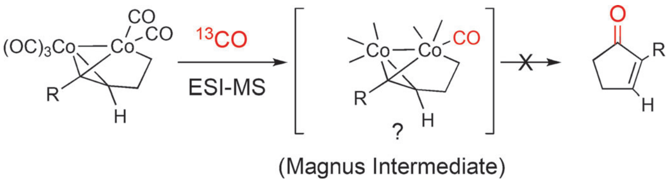
Mind the gap: Band-structure calculations on a series of nano- and sub-nano sized cobalt(II)-polyoxotitanium cages reveal that the molecular dipole moment can have an unexpected effect on the band gap (see scheme; CB = conduction band, VB = valence band). This ability to decrease the band gap provides a strategy for the formation of low-band-gap cages.



Reaction Mechanisms

D. Lesage, A. Milet, A. Memboeuf, J. Blu,
A. E. Greene, J.-C. Tabet,
Y. Gimbert* **1939 – 1942**

The Pauson–Khand Mechanism Revisited: Origin of CO in the Final Product

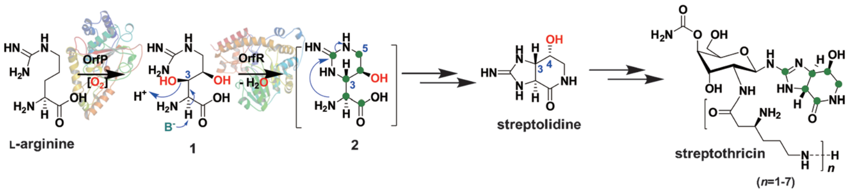


The CO–Co connection: The existence of a commonly accepted Magnus intermediate in the Pauson–Khand reaction has been disproven through mass spectrometry experiments with ^{13}CO. In such experiments the expected labeled cyclopentenone was not detected. Alternative reaction pathways are advanced from theoretical studies.

Biosynthetic Pathways

C. Y. Chang, S. Y. Lyu, Y. C. Liu, N. S. Hsu,
C. C. Wu, C. F. Tang, K. H. Lin, J. Y. Ho,
C. J. Wu, M. D. Tsai, T. L. Li* **1943 – 1948**

Biosynthesis of Streptolidine Involved Two Unexpected Intermediates Produced by a Dihydroxylase and a Cyclase through Unusual Mechanisms

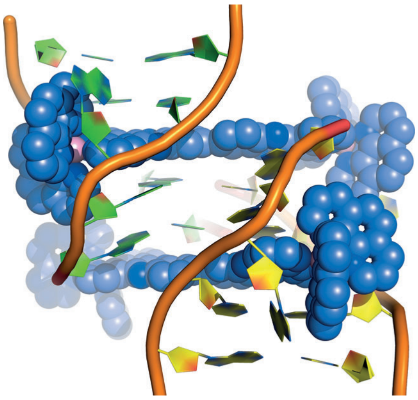


Green label: In streptolidine biosynthesis, OrfP catalyzes the Fe^{II}-dependent double hydroxylation of L-Arg to form **1**, which is undergoes a PLP-dependent cyclization reaction catalyzed by OrfR to form **2**. The longstanding question of the streptolidine biosynthesis was solved by the incorporation of [$^{13}C_6$]-**2** (green dots are ^{13}C) into streptothricin by a feeding experiment.

DNA Metalloinsertors

D. R. Boer, L. Wu, P. Lincoln,*
M. Coll* **1949 – 1952**

Thread Insertion of a Bis(dipyridophenazine) Diruthenium Complex into the DNA Double Helix by the Extrusion of AT Base Pairs and Cross-Linking of DNA Duplexes

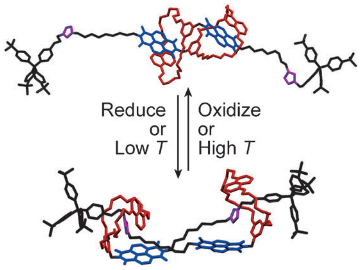


Pinned together by molecular rivets: The crystal structure of the complex between double-stranded DNA and the binuclear complex [μ-(11,11′-bidppz)(1,10-phenanthroline)$_4$Ru$_2$]$^{4+}$ (**1**, shown in blue; bidppz = bis(dipyridophenazine)), showed that one half of the bidppz ligand inserts into a DNA duplex, and the other half stacks onto the blunt end of a nearby DNA duplex. Two molecules of **1** with the same binding mode effectively cross-link two DNA duplexes.

Molecular Switches

C. J. Bruns, J. Li, M. Frasconi,
S. T. Schneebeli, J. Iehl,
H.-P. Jacquot de Rouville, S. I. Stupp,
G. A. Voth,* J. F. Stoddart* **1953 – 1958**

An Electrochemically and Thermally Switchable Donor–Acceptor [*c*2]Daisy Chain Rotaxane

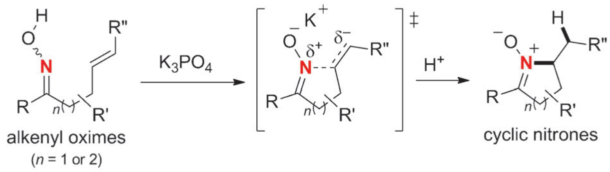


Flexing molecular muscles: A bistable [*c*2]daisy chain rotaxane, based on π-associated donor–acceptor interactions between naphthalene diimide and dioxynaphthalene recognition units, is obtained using click chemistry. A combination of experimental data and molecular dynamics simulations demonstrates that the daisy chain's extensile and contractile motions can be controlled, either by redox chemistry (a thermodynamically driven process), or by temperature (an entropy-driven process).

Hydroamination

X. Peng, B. M. K. Tong, H. Hirao,*
S. Chiba* **1959 – 1962**

Inorganic-Base-Mediated Hydroamination of Alkenyl Oximes for the Synthesis of Cyclic Nitrones

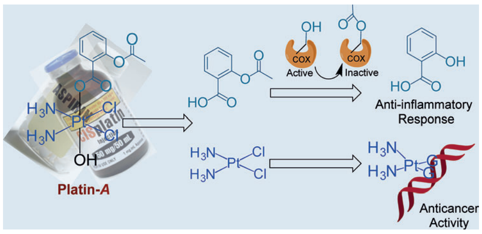


Basic ring building: A method for the synthesis of cyclic nitrones by using alkenyl oximes was developed based on hydroamination mediated by an inorganic base. DFT calculations for the reaction pathway suggested that this hydroamination could proceed through nucleophilic amination of the unactivated alkene by the oxime nitrogen atom, with the transition state stabilized by ionic interaction with a metal cation such as K$^+$.

Antitumor Agents

R. K. Pathak, S. Marrache, J. H. Choi, T. B. Berding, S. Dhar* ____ **1963 – 1967**

The Prodrug Platin-*A*: Simultaneous Release of Cisplatin and Aspirin

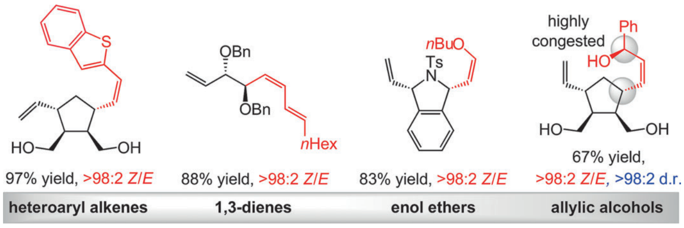


The prodrug Platin-*A* was designed to release cisplatin and aspirin to ameliorate the side effects of cisplatin. Platin-*A* exhibits anticancer and anti-inflammatory properties which are better than those for the combined use of cisplatin and aspirin. These findings highlight the advantages of combining anti-inflammatory treatment with chemotherapy when both the drugs are delivered as a single prodrug.

Olefin Metathesis

M. J. Koh, R. K. M. Khan, S. Torker, A. H. Hoveyda* ____ **1968 – 1972**

Broadly Applicable *Z*- and Diastereoselective Ring-Opening/Cross-Metathesis Catalyzed by a Dithiolate Ru Complex

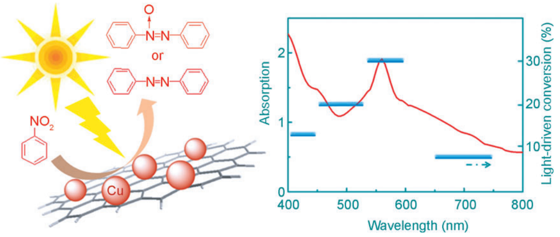


Finally, the full range: For the first time, Ru-catalyzed olefin metathesis transformations with heteroaryl-substituted alkenes, 1,3-dienes, enol ethers, and allylic and homoallylic alcohols can be performed efficiently and often with > 98 % *Z* selectivity. Hydrogen bonding with the dithiolate ligand likely facilitates ring-opening/cross-metathesis reactions of allylic alcohols.

Photochemistry

X. N. Guo, C. H. Hao, G. Q. Jin, H. Y. Zhu,* X. Y. Guo* ____ **1973 – 1977**

Copper Nanoparticles on Graphene Support: An Efficient Photocatalyst for Coupling of Nitroaromatics in Visible Light

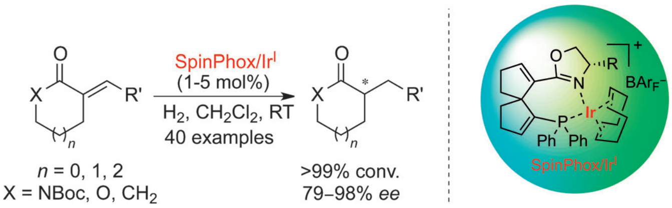


Green, light-assisted catalysis: Graphene-supported copper nanoparticles are used as photocatalysts. The photocatalysts can controllably reduce nitroaromatics to corresponding azoxy and azo compounds (see picture) under visible-light irradiation.

Asymmetric Catalysis

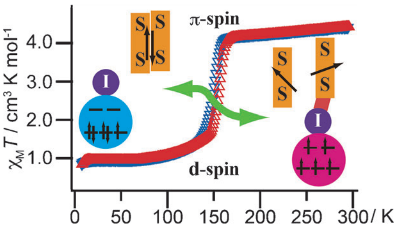
X. Liu, Z. Han, Z. Wang, K. Ding* ____ **1978 – 1982**

SpinPhox/Iridium(I)-Catalyzed Asymmetric Hydrogenation of Cyclic α-Alkylidene Carbonyl Compounds



Take it for a spin: SpinPhox/Ir$^{\mathrm{I}}$ complexes are highly efficient and versatile in the enantioselective hydrogenation of a broad spectrum of exocyclic α,β-unsaturated carbonyl compounds, especially the challenging α-alkylidene lactam substrates with six- or seven-membered rings. The synthetic utility of the present protocol is demonstrated in the asymmetric synthesis of biologically important loxoprofen and ε-aminocaproic acid derivatives.

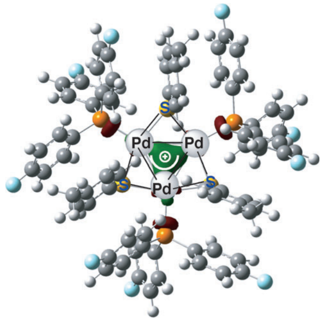
Something to get crossover: An Fe^{III} complex with iodine-substituted ligands involving a paramagnetic nickel dithiolene anion shows a synergy between a spin-crossover transition and a spin-Peierls-like singlet formation. The halogen-bond interactions between the iodine and the sulfur atoms stabilized the paramagnetic state of π-spins and played a significant role in the synergistic magnetic transition between d- and π-spins.



Spin Crossover

K. Fukuroi, K. Takahashi,* T. Mochida, T. Sakurai, H. Ohta, T. Yamamoto, Y. Einaga, H. Mori ________ **1983 – 1986**

Synergistic Spin Transition between Spin Crossover and Spin-Peierls-like Singlet Formation in the Halogen-Bonded Molecular Hybrid System: $[Fe(Iqsal)_2][Ni(dmit)_2]\cdot CH_3CN\cdot H_2O$

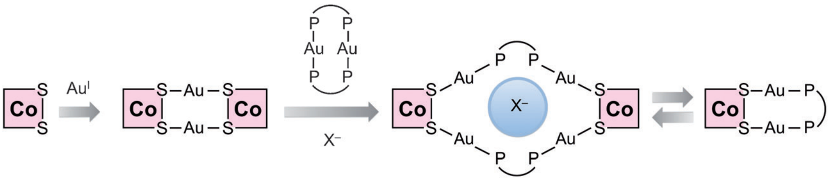


Pd trifecta: C_3-symmetric cationic triangular palladium clusters $[\{(SAr')(PAr_3)Pd\}_3]^+$ were prepared by activation of the C–S bond of isothioureas. These complexes are the first noble-metal analogues of the π-aromatic cyclopropenyl cation $[C_3H_3]^+$.

Aromaticity

S. Blanchard, L. Fensterbank, G. Gontard, E. Lacôte, G. Maestri,* M. Malacria ________ **1987 – 1991**

Synthesis of Triangular Tripalladium Cations as Noble-Metal Analogues of the Cyclopropenyl Cation



($X^- = BF_4^-, ClO_4^-, ReO_4^-$)

The eight-membered $Au^I_2Co^{III}_2$ metallaring in $[Au_2Co_2(D\text{-}nmp)_4]$ (D-nmp = *N*-methyl-D-penicillaminate) was synthesized from $[Co(D\text{-}nmp)_2]^-$ and a gold(I) precursor. By treatment with $[Au_2(dppe)_2]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane), this metallaring could be rationally expanded to the eighteen-membered $Au^I_4Co^{III}_2$ metallaring in $[Au_4Co_2(dppe)_2(D\text{-}nmp)_4]^{2+}$, which also accommodates a tetrahedral anion inside the ring.

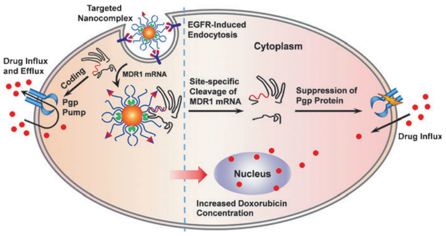
Metallaligands

K. Oji, A. Igashira-Kamiyama, N. Yoshinari, T. Konno* ____ **1992 – 1996**

Formation, Expansion, and Interconversion of Metallarings in a Sulfur-Bridged Au^ICo^{III} Coordination System

Biomimetics

Back Cover



RISC management: Synthetic RISC-mimic nanocomplexes have been developed for sequence-specific gene silencing. The nanocomplexes, which were designed to target multidrug resistance, were shown to effectively suppress Pgp expression and thus restore drug sensitivity in OVCAR8/ADR cells to Pgp-transportable cytotoxic agents.

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

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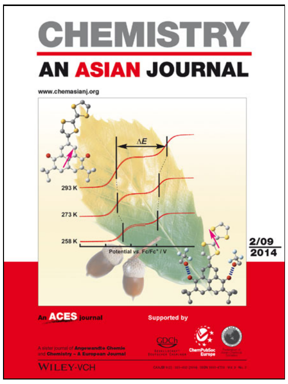

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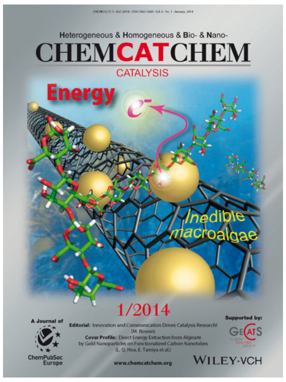

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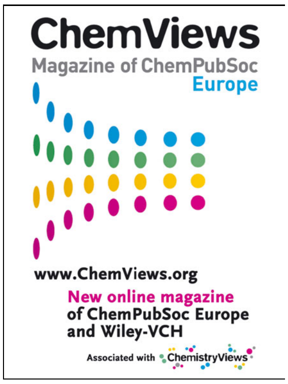

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