



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at [www.angewandte.org](http://www.angewandte.org) soon:

T. A. Rokob, A. Hamza, A. Stirling, T. Soós,\* I. Pápai\*  
**Turning Frustration into Bond Activation: A Theoretical  
 Mechanistic Study on Heterolytic Hydrogen Splitting by  
 Frustrated Lewis Pairs**

E. Stavitski, M. H. Kox, I. Swart, F. M. de Groot, B. M. Weckhuysen\*  
**In Situ Synchrotron-Based IR Microspectroscopy To Study  
 Catalytic Reactions in Zeolite Crystals**

C. Ruspic, J. R. Moss, M. Schürmann, S. Harder\*  
**Remarkable Stability of Metallocenes with Superbulky Ligands:  
 Spontaneous Reduction of Sm<sup>III</sup> to Sm<sup>II</sup>**

L. M. Fidalgo, G. Whyte, D. Bratton, C. F. Kaminski, C. Abell,  
 W. T. S. Huck\*

**From Microdroplets to Microfluidics: Selective Emulsion  
 Separation in Microfluidic Devices**

I. Paterson,\* E. A. Anderson, S. M. Dalby, J. Ho Lim, J. Genovino,  
 P. Maltas, C. Moessner

**Total Synthesis of Spirastrellolide A Methyl Ester—Part 1:  
 Synthesis of an Advanced C17–C40 Bis(spiroacetal) Subunit**

I. Paterson,\* E. A. Anderson, S. M. Dalby, J. Ho Lim, J. Genovino,  
 P. Maltas, C. Moessner

**Total Synthesis of Spirastrellolide A Methyl Ester—Part 2:  
 Subunit Union and Completion of the Synthesis**

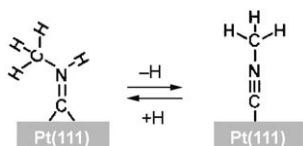
Essentials of Carbohydrate Chemistry and Biochemistry Thisbe K. Lindhorst

Quality Assurance for the Analytical Chemistry Laboratory D. Brynn Hibbert

## Books

reviewed by A. Hoffmann-Röder — 1360

reviewed by M. Vogel — 1360



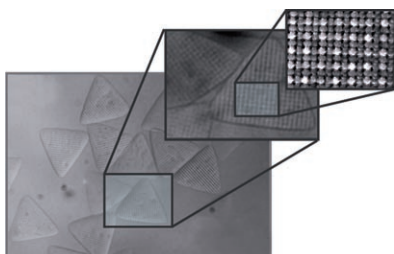
**Realization of a dream:** The scanning tunneling microscope is not only capable of imaging and manipulating adsorbed species, it can be used for vibrational spectroscopy on these species. With this method, a full reaction cycle was investigated in which methylaminocarbene on Pt(111) was dehydrogenated and rehydrogenated (see scheme). This method is expected to be instrumental in the understanding of fundamental phenomena in heterogeneous catalysis.

## Highlights

### Surface Chemistry

C. Wöll\* — 1364–1366

Spectroscopic Characterization and Deliberate Modification of a Single Molecule by Tunneling of Electrons



**Assembly-line microparticles:** An innovative approach for the high-throughput fabrication of complex three-dimensional and chemically anisotropic microstructures is highlighted (illustrated: patterned triangles with edges of circa 60 μm) based on the synergistic use of stop-flow interference lithography and microfluidics.

### Microfabrication

R. S. Kane\* — 1368–1370

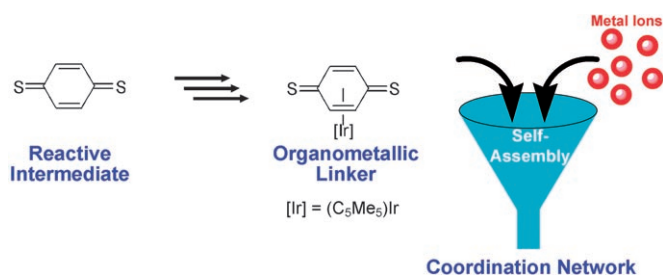
Fabricating Complex Polymeric Micro- and Nanostructures: Lithography in Microfluidic Devices

## Minireviews

### Supramolecular Assemblies

J. Moussa, H. Amouri\* — 1372–1380

Supramolecular Assemblies Based on Organometallic Quinonoid Linkers: A New Class of Coordination Networks



**A new family** of coordination networks self-assembles from individual components using metalated quinonoid and thioquinonoid linkers (see scheme). These novel assemblies exhibit short  $\pi$ – $\pi$

and M...M interactions. The wide range of new architectures illustrates the role of the organometallic linkers in promising compounds for the development of functional materials.

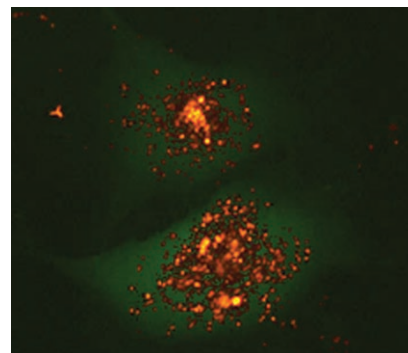
## Reviews

### Nucleic Acid Carriers

V. Sokolova, M. Epple\* — 1382–1395

Inorganic Nanoparticles as Carriers of Nucleic Acids into Cells

**Particularly useful:** Many different kinds of nanoparticles are readily taken up by living cells (see picture; nanoparticles can be seen as red dots inside the cell) and thereby can be used as carriers for nucleic acids (DNA, siRNA) to change the genetic arsenal of a cell. Clinically, this is of interest to treat genetically caused diseases (so called “gene therapy”).



## Communications

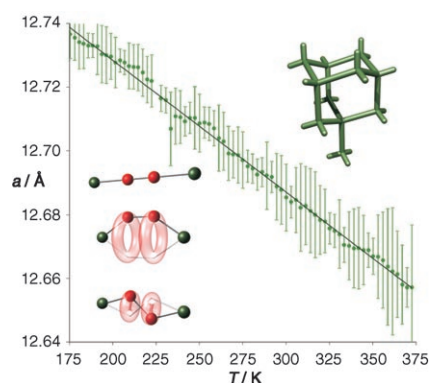
### Negative Thermal Expansion

A. E. Phillips, A. L. Goodwin, G. J. Halder, P. D. Southon, C. J. Kepert\* — 1396–1399



Nanoporosity and Exceptional Negative Thermal Expansion in Single-Network Cadmium Cyanide

**Accentuate the negative:** Single-network cadmium cyanide displays isotropic negative thermal expansion behavior of unprecedented magnitude over a large temperature range (see graph of unit cell parameter  $a$  versus temperature). Guest molecules in the pores of this framework block the transverse vibrational modes responsible for this behavior, causing the value of the linear coefficient of thermal expansion to increase with guest occupancy.

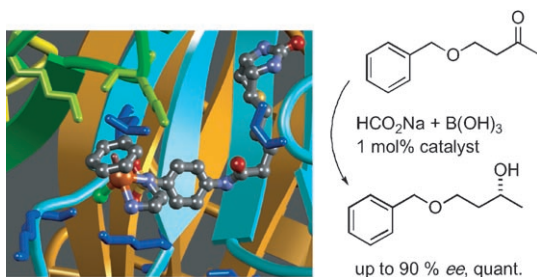


### For the USA and Canada:

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electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



### Artificial Metalloenzymes

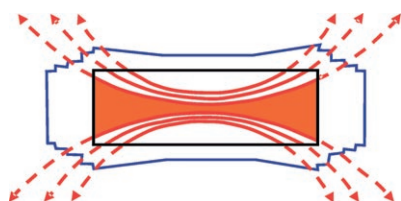
M. Creus, A. Pordea, T. Rossel, A. Sardo,  
C. Letondor, A. Ivanova, I. LeTrong,  
R. E. Stenkamp,\*  
T. R. Ward\* \_\_\_\_\_ 1400–1404

X-Ray Structure and Designed Evolution  
of an Artificial Transfer Hydrogenase



**A structure is worth a thousand words:**  
Guided by the X-ray structure of an *S*-selective artificial transfer hydrogenase, designed evolution was used to optimize the selectivity of hybrid catalysts. Fine-tuning of the second coordination sphere

of the ruthenium center (see picture, orange sphere) by introduction of two point mutations allowed the identification of selective artificial transfer hydrogenases for the reduction of dialkyl ketones.

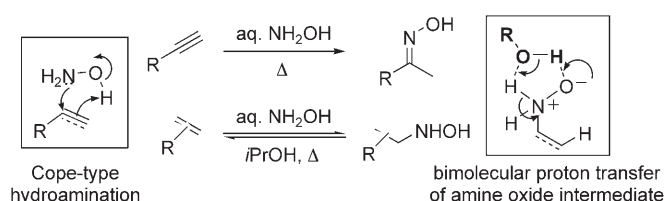


**Taking shape:** The 3D arrangement of a biomimetic fluorapatite–gelatine composite consists of elementary dipoles on the nanometer scale. The dipole field developed during growth of the composite causes formation and inclusion of gelatine microfibrils, which line up in the direction of the developing electric field. This microfibril pattern is the intrinsic code for development from an elongated hexagonal prism into a dumbbell morphology (see picture).

### Biomimetalization

R. Kniep,\* P. Simon \_\_\_\_\_ 1405–1409

“Hidden” Hierarchy of Microfibrils within  
3D-Periodic Fluorapatite–Gelatine  
Nanocomposites: Development of  
Complexity and Form in a Biomimetic  
System



**Keep it simple!** Intermolecular hydroamination can be achieved simply upon heating alkynes and alkenes with aqueous hydroxylamine. Alkynes react to afford oximes in good to excellent yields, and the

formation of Markovnikov products is favored. A mechanism involving Cope-type hydroamination followed by bimolecular proton transfer is suggested and supported by DFT studies.

### Hydroamination

A. M. Beauchemin,\* J. Moran,  
M.-E. Lebrun, C. Séguin, E. Dimitrijevic,  
L. Zhang, S. I. Gorelsky \_\_\_\_\_ 1410–1413

Intermolecular Cope-Type  
Hydroamination of Alkenes  
and Alkynes



# Incredibly *inexpensive!*



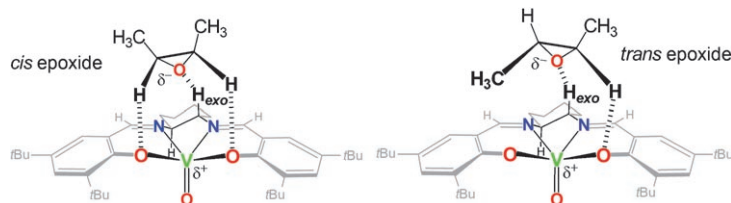
Do chemistry journals really cost so much? Perhaps some do, but certainly not *Angewandte Chemie*! In 2006, an entire institution could subscribe through Wiley InterScience for about 4000 Euro and get access to 48 issues with over 1600 articles and all associated online search options, and for just 10% more, the printed issues could be included as well. For full members of the German Chemical Society (GDCh), a personal subscription cost not even 300 Euro, and student GDCh members paid less than 140 Euro, which is just under 3 Euro per issue – a price that even compares with high-circulation newsstand publications!



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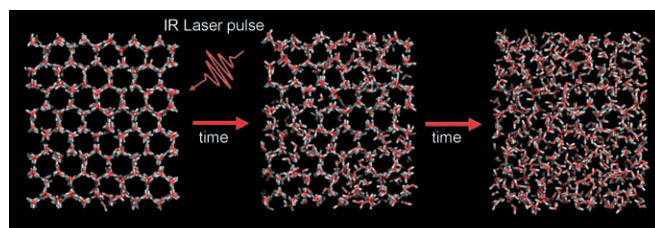
**EPR and ENDOR spectroscopies** combined with DFT calculations have revealed the selective binding of a *cis* over a *trans* epoxide to a chiral vanadyl salen complex (see picture). Complementary DFT calculations identified a weak electrostatic

interaction supplemented by multiple hydrogen-bonding contacts as the origins of this selectivity. These observations were experimentally confirmed in frozen solution by orientation selective ENDOR measurements.

### ENDOR spectroscopy

D. M. Murphy,\* I. A. Fallis,\* D. J. Willock,\* J. Landon, E. Carter, E. Vinck **1414–1416**

Discrimination of Geometrical Epoxide Isomers by ENDOR Spectroscopy and DFT Calculations: The Role of Hydrogen Bonds



**Cold as ice:** Molecular dynamics simulation provides snapshots of a melting ice crystal (see picture). The laser pulse heats up the system, and the energy is absorbed in the OH bonds. After a few picoseconds, the energy is transferred to rotational and

translational energy, causing the crystal to melt. The melting starts as a nucleation process, and even long after the first melting is initialized, pockets of crystal-line structures can be found.

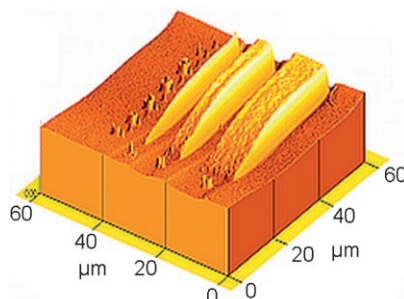
### Molecular Dynamics Simulations

C. Caleman, D. van der Spoel\* **1417–1420**

Picosecond Melting of Ice by an Infrared Laser Pulse: A Simulation Study



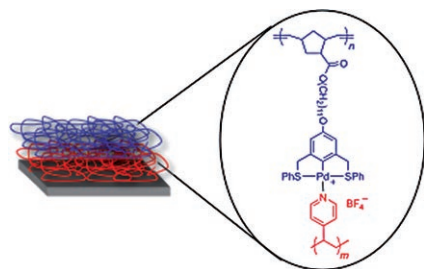
**Nanopatterns:** The feasibility of a new lithographic technique, chemical lithography with self-assembled monolayers (SAMs) of commercially available aliphatic compounds as resist materials, is demonstrated by the fabrication of polymer nanopatterns (see image). The technique is based on an irradiation-promoted exchange reaction. Patterning requires a much lower dose than electron-beam chemical lithography with aromatic SAMs as resists.



### Chemical Lithography

N. Ballav, S. Schilp, M. Zharnikov\* **1421–1424**

Electron-Beam Chemical Lithography with Aliphatic Self-Assembled Monolayers



**Metal–ligand interactions** can be used to create coordination polymer multilayers (see picture). Growth is linear with layer and bilayer number, and the bilayer thickness depends on deposition concentration. This approach combines the stability of covalent multilayers with the responsiveness of polyelectrolyte-based multilayers.

### Polymer Multilayers

C. R. South, V. Piñón III, M. Weck\* **1425–1428**

Erasable Coordination Polymer Multilayers on Gold



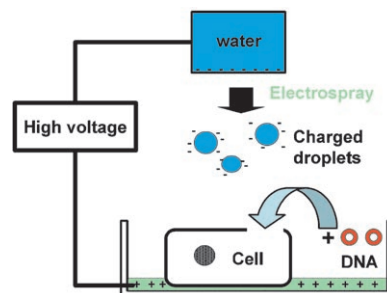


## Biotechnology

Y. Okubo, K. Ikemoto,\* K. Koike,  
C. Tsutsui, I. Sakata, O. Takei, A. Adachi,  
T. Sakai\* 1429–1431

DNA Introduction into Living Cells by  
Water Droplet Impact with an Electrospray  
Process

**Charged water droplets** from an electro-spray device can generate a transient hole in cell membranes for DNA transport into a living cell. The number of cells containing DNA encoded with green fluorescent protein (GFP) increases with an increase in applied voltage. The technique can be applied to gene transfection to eukaryotic cells, tissues, and prokaryotic cells.

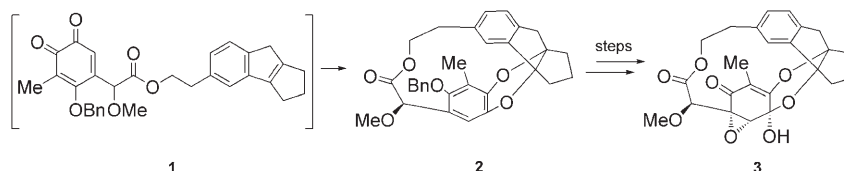


## Natural Product Synthesis

K. C. Nicolaou,\* J. Wang,  
Y. Tang 1432–1435



Synthesis of the Sporolide Ring  
Framework through a Cascade Sequence  
Involving an Intramolecular  
[4+2] Cycloaddition Reaction of an  
*o*-Quinone



**Sea-ing is believing:** The *o*-quinone indene intermediate **1** was generated from the corresponding catechol substrate and converted into macrocycle **2** by a cascade sequence involving a novel intramolecular [4+2] cycloaddition reaction. This

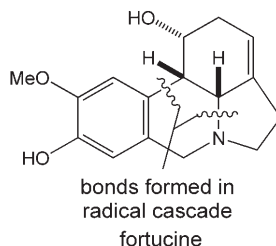
sequence serves as the key process to form the core heptacyclic structure **3** of the marine-derived natural products sporolide A and B, which were isolated from the relevant actinomycete fermentation broths.

## Natural Product Synthesis

A. Biechy, S. Hachisu, B. Quiclet-Sire,  
L. Ricard, S. Z. Zard\* 1436–1438



The Total Synthesis of (±)-Fortucine and a  
Revision of the Structure of Kirkine



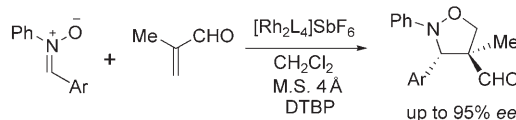
**A molecular zipper:** The total synthesis of the natural product fortucine relies on a radical cascade process initiated by the generation of a nitrogen-centered (amidyl) radical (see picture). The procedure is concise, and tin-free, as well as stereo- and regioselective. This synthesis has enabled the correction of the structure of kirkine, and the strategy represents a general and rapid entry into the galanthan framework.

## Asymmetric Catalysis

Y. Wang, J. Wolf, P. Zavalij,  
M. P. Doyle\* 1439–1442

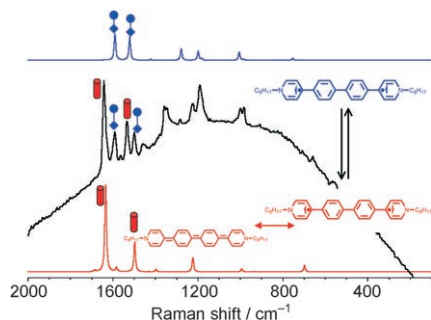


Cationic Chiral Dirhodium  
Carboxamidates Are Activated  
for Lewis Acid Catalysis



**The power of a positive charge:** Oxidized chiral dirhodium carboxamidate salts increase the rate of reaction of selected aldehydes with the Danishefsky diene (hetero-Diels–Alder reaction) and with nitrones (1,3-dipolar cycloaddition; see

scheme, L = (*R*)-menthyl-2-oxopyrrolidine-(5*S*)-carboxylate, DTBP = 2,6-di-*tert*-butylpyridine). These cationic catalysts enhance enantiocontrol relative to their neutral dirhodium(II) counterparts.

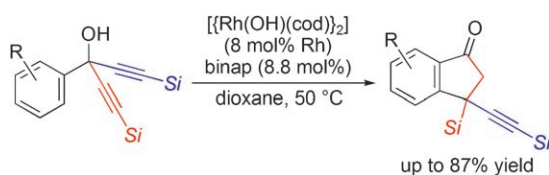


**Raman marks** of the singlet and triplet biradical species of an extended viologen are resolved in spite of the efficient intersystem crossing promoted by the quasi-isoenergetic locations of the lowest singlet and triplet states. Variable-temperature Raman measurements (see spectra) are instrumental for discriminating between the species, which rapidly interconvert their spin states.

### Raman Detection of Biradicals

J. Casado,\* S. Patchkovskii,\*  
M. Z. Zgierski, L. Hermosilla, C. Sieiro,  
M. Moreno Oliva,  
J. T. López Navarrete\* — 1443–1446

Raman Detection of “Ambiguous”  
Conjugated Biradicals: Rapid Thermal  
Singlet-to-Triplet Intersystem Crossing  
in an Extended Viologen



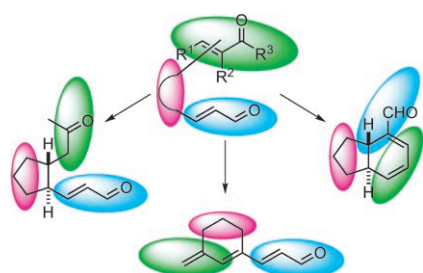
**Ten little indanones:** The title reaction (see scheme; Si = trialkylsilyl) is proposed to go through a pathway involving a  $\beta$ -carbon elimination/carborhodation sequence. Ready access to the carbinol

substrates from an aromatic ester and a terminal alkyne makes the present catalysis reaction an efficient way of preparing 3-alkynyl-1-indanones.

### Carborhodation

R. Shintani,\* K. Takatsu, T. Katoh,  
T. Nishimura, T. Hayashi\* — 1447–1449

Rhodium-Catalyzed Rearrangement of  
Aryl Bis(alkynyl) Carbinols to  
3-Alkynyl-1-indanones

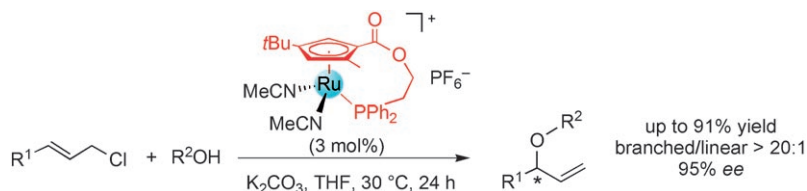


**Various linked unsaturated dicarbonyl compounds** were cyclized by dienamine catalysis. Depending on the substrates, alternative pathways were observed, leading to mono- and bicyclic products in high enantiomeric excess.

### Asymmetric Synthesis

R. M. de Figueiredo, R. Fröhlich,  
M. Christmann\* — 1450–1453

Amine-Catalyzed Cyclizations of Tethered  
 $\alpha,\beta$ -Unsaturated Carbonyl Compounds



**Design of an asymmetric catalyst:** The planar-chiral cyclopentadienyl ruthenium complex shown in the scheme effectively catalyzes the reactions of unsymmetrically

substituted allyl halides with phenol and alcohol to give the corresponding branched allyl ethers with high regio- and enantioselectivity.

### Asymmetric Catalysis

K. Onitsuka,\* H. Okuda,  
H. Sasai — 1454–1457

Regio- and Enantioselective O-Allylation  
of Phenol and Alcohol Catalyzed by a  
Planar-Chiral Cyclopentadienyl  
Ruthenium Complex

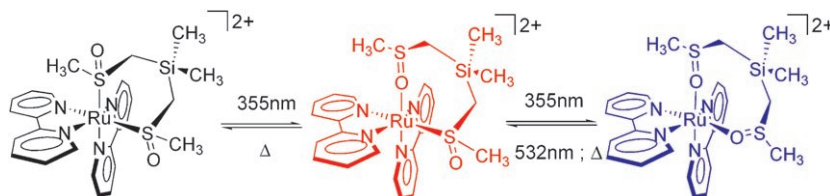


## Photochromic Complexes

N. V. Mockus, D. Rabinovich,  
J. L. Petersen, J. J. Rack\* — 1458 – 1461



Femtosecond Isomerization in a  
Photochromic Molecular Switch



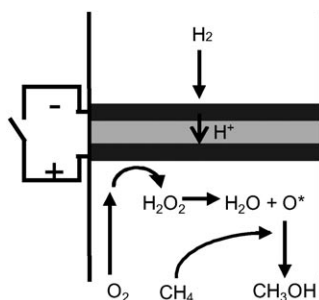
**Back and forth:** Irradiation in the metal-to-ligand charge transfer band of the bis S-bonded complex shown (see scheme, left) yields the mixed S,O isomer and then the O,O isomer in two subsequent excited-state reactions. Excitation of the S,O

isomer at 355 nm yields the O,O isomer, while 532-nm excitation of the O,O isomer yields the S,O isomer. Isomerization occurs on a femto- to picosecond time-scale, demonstrating two-color photonic switching.

## Methane Oxidation

A. Tomita, J. Nakajima,  
T. Hibino\* — 1462 – 1464

Direct Oxidation of Methane to Methanol  
at Low Temperature and Pressure in an  
Electrochemical Fuel Cell

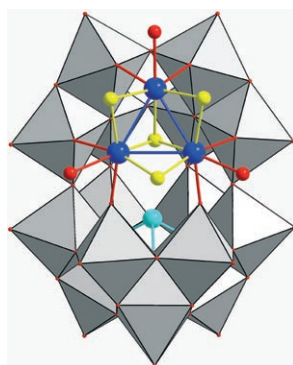


**Fuel for thought?** The direct oxidation of methane to methanol occurs at atmospheric pressure between 50 and 250 °C in a fuel-cell-type reactor (see picture). The efficiency of the electrochemical activation of oxygen is higher than that for the catalytic activation of oxygen.

## Polythiooxometalates

M. N. Sokolov, I. V. Kalinina,  
E. V. Peresypkina, E. Cadot, S. V. Tkachev,  
V. P. Fedin\* — 1465 – 1468

Incorporation of Molybdenum Sulfide  
Cluster Units into a Dawson-Like  
Polyoxometalate Structure To Give  
Hybrid Polythiooxometalates



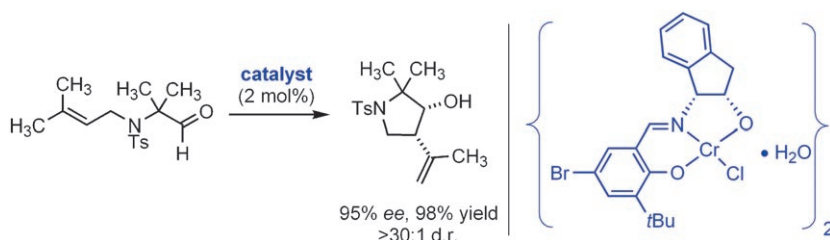
**Hybrid polyoxometalates (POMs)**  
[AsW<sub>15</sub>Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>O<sub>53</sub>]<sup>9-</sup> and  
[AsW<sub>15</sub>Mo<sub>3</sub>O<sub>2</sub>S<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>O<sub>53</sub>]<sup>9-</sup> in which a  
chalcogenide cluster unit is incorporated  
into a classical POM structure have been  
prepared and characterized by X-ray analysis  
and <sup>183</sup>W NMR spectroscopy. The structure  
of the former can be derived from that of  
[H<sub>2</sub>AsW<sub>18</sub>O<sub>60</sub>]<sup>7-</sup> by replacing one of the  
six {W<sub>3</sub>O<sub>13</sub>} units by a {Mo<sub>3</sub>S<sub>4</sub>O<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>}  
unit (see picture; As cyan, Mo blue, O red,  
S yellow).

## Cyclizations

M. L. Grachan, M. T. Tudge,  
E. N. Jacobsen\* — 1469 – 1472



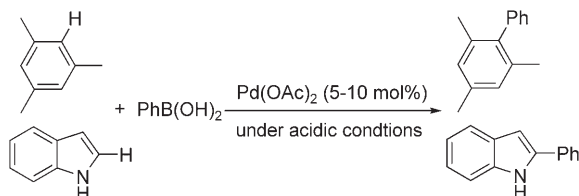
Enantioselective Catalytic Carbonyl–Ene  
Cyclization Reactions



**Intramolecular ene reactions** of simple  
alkenyl aldehydes are catalyzed by a chiral  
(Schiff base)Cr<sup>III</sup> complex with high enan-  
tio- and diastereoselectivity, affording  
densely functionalized heterocyclic or

carbocyclic products (see scheme for  
example). Desymmetrizations of alkenyl  
dialdehydes and bis(alkenyl) aldehydes  
are also achieved.





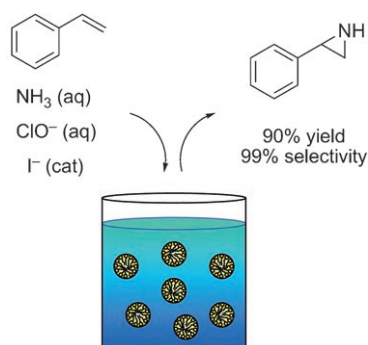
**No compass required:** A method is described for forming biaryl C–C bonds by a Pd<sup>II</sup>-catalyzed cross-coupling of aryl C–H bonds with aryl boronic acids under mild conditions without the presence of directing groups. Different substituents

on both (hetero)arenes and aryl boronic acids are compatible with the reaction conditions, and the homocoupling of boronic acids is highly inhibited. Dioxygen was applied as the final oxidant.

### C–H Activation

S.-D. Yang, C.-L. Sun, Z. Fang, B.-J. Li, Y.-Z. Li, Z.-J. Shi\* **1473–1476**

Palladium-Catalyzed Direct Arylation of (Hetero)Arenes with Aryl Boronic Acids

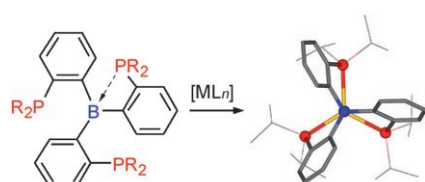


**Aziridines from ammonia:** Unprotected aziridines are formed from styrenes in one catalytic step. Ammonia is incorporated directly using an aqueous micellar solution containing bleach as oxidant and substoichiometric amounts of iodide (see picture).

### Aziridination

C. Varszegi, M. Ernst, F. van Laar, B. F. Sels, E. Schwab, D. E. De Vos\* **1477–1480**

A Micellar Iodide-Catalyzed Synthesis of Unprotected Aziridines from Styrenes and Ammonia

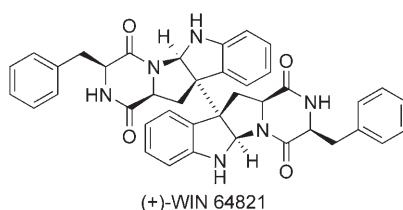


**Symmetry from within:** Coordination of a triphosphenyl-borane ligand to gold(I) and platinum(0) affords metallaboratranes exhibiting C<sub>3</sub> symmetry both in solution and in the solid state. Such a helical geometry is supported by axial M→B dative interactions and results from the envelope conformations of the PCCBM metallacycles.

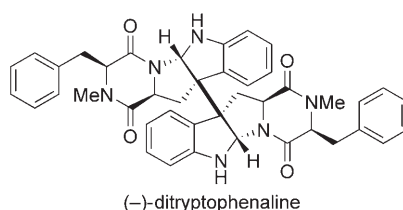
### Ambiphilic Ligands

S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron,\* O. V. Ozerov,\* D. Bourissou\* **1481–1484**

Metallaboratranes Derived from a Triphosphenyl-Borane: Intrinsic C<sub>3</sub> Symmetry Supported by a Z-Type Ligand



**On a fast track:** The secondary metabolites (+)-WIN 64821 and (–)-ditryptophenaline have been synthesized in six and seven steps, respectively, from amino acid derivatives in a concise and enantioselective manner. The gram-scale synthesis



of key intermediates and the simultaneous introduction of vicinal quaternary stereocenters are described. The synthesis and structural confirmation of (–)-1'-(2-phenylethylene)ditryptophenaline is also reported.

### Natural Product Synthesis

M. Movassaghi,\* M. A. Schmidt, J. A. Ashenhurst **1485–1487**

Concise Total Synthesis of (+)-WIN 64821 and (–)-Ditryptophenaline

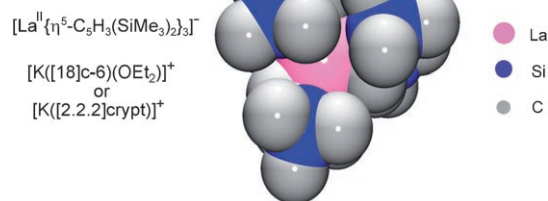


## Lanthanum(II) Compounds

P. B. Hitchcock, M. F. Lappert,\*  
L. Maron,\*  
A. V. Protchenko\* — 1488 – 1491



Lanthanum Does Form Stable Molecular Compounds in the +2 Oxidation State



**Getting down to business:** Reduction of the La<sup>III</sup> tricyclopentadienide complex [LaCp''<sub>3</sub>] (Cp'' = η<sup>5</sup>-1,3-(SiMe<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>) by K and [18]crown-6 or [2,2,2]cryptand produced thermally stable mononuclear crystalline lanthanate(II) salts. The La

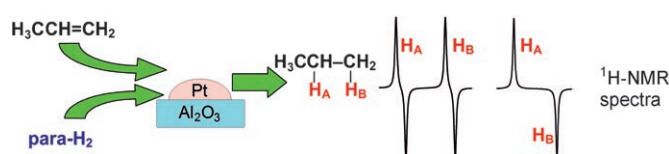
+2 oxidation state in these complexes was confirmed both in solution (EPR) and the solid state (EPR, SQUID, X-ray diffraction) and was supported by a computational study.

## Heterogeneous Catalysis

K. V. Kovtunov, I. E. Beck, V. I. Bukhtiyarov,  
I. V. Koptug\* — 1492 – 1495



Observation of Parahydrogen-Induced Polarization in Heterogeneous Hydrogenation on Supported Metal Catalysts



**Contrary to popular opinion**, two H atoms from the same H<sub>2</sub> molecule can end up in the same product molecule and retain their spin correlation during heterogeneous hydrogenation on supported metal catalysts and thus produce parahydrogen-

induced nuclear spin polarization in the reaction products (see picture). For 0.6-nm Pt clusters on alumina, the contribution of the pairwise addition route in the hydrogenation of propylene amounts to at least 3%.

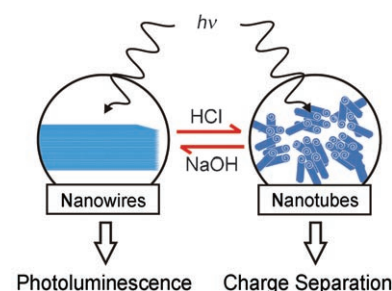
## Nanostructures

A. Riss, T. Berger, S. Stankic, J. Bernardi,  
E. Knözinger, O. Diwald\* — 1496 – 1499



Charge Separation in Layered Titanate Nanostructures: Effect of Ion Exchange Induced Morphology Transformation

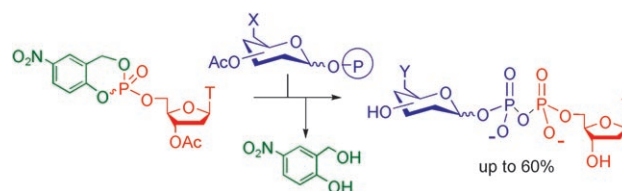
**Clear complementarity:** Surface chemistry induced morphology transformation in layered titanate nanostructures can be used to control their photoelectronic properties. Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nanowires can be transformed reversibly into nanotubes with acid/base treatment (see picture); the nanowires exhibit photoluminescence, which is suppressed in the nanotubes, while the charge separation is stronger in the nanotubes.



## Carbohydrate Synthesis

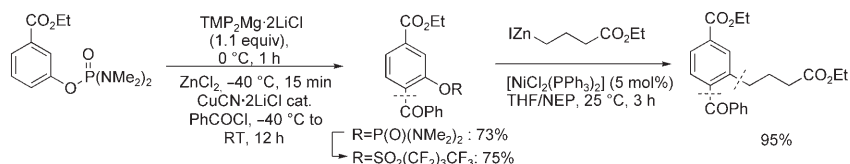
S. Wendicke, S. Warnecke,  
C. Meier\* — 1500 – 1502

Efficient Synthesis of Nucleoside Diphosphate Glycopyranoses



**Short and sweet:** A new, short synthetic pathway for the synthesis of the enormously important class of nucleoside diphosphate sugars (NDP sugars) was developed using *cyclo*-saligenyl (*cyclo*Sal) nucleosyl phosphate triesters as active

ester equivalents that form the target compounds in the presence of anomerically pure pyranose 1-phosphates in high yields (see scheme; T = thymine; X = OAc, H; Y = OH, H).



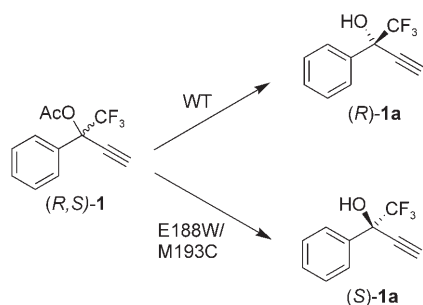
## Grignard Reactions

C. J. Rohbogner, G. C. Clososki,  
P. Knochel\* 1503–1507

A General Method for *meta* and *para*  
Functionalization of Arenes Using  
 $\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$

**Getting directions:** The  $(\text{Me}_2\text{N})_2\text{P}(\text{O})\text{O}$  substituent serves as an effective directing-metalation group in the magnesiation of substituted arenes with  $\text{TMP}_2\text{Mg} \cdot 2\text{LiCl}$  (see scheme). This reaction can be used

to achieve difficult substitution patterns by *meta,para* or *para,meta* functionalization. TMP = 2,2,6,6-tetramethylpiperamidy, NEP = N-ethylpyrrolidone.



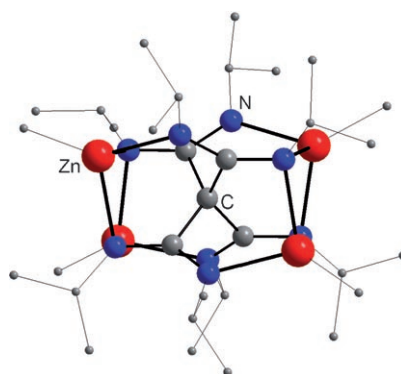
**Simultaneous saturation mutagenesis** at three amino acid residues of esterase BS2 followed by high-throughput screening identified a double mutant (E188W/M193C) with inverted enantioselectivity, high  $E$  values, and broadened substrate range compared to the wild-type (WT) enzyme, while the single mutants lacked this property. The kinetic resolution of ester **1** with the enzymes is shown in the scheme.

## Esterases

S. Bartsch, R. Kourist,  
U. T. Bornscheuer\* 1508–1511

Complete Inversion of Enantioselectivity  
towards Acetylated Tertiary Alcohols by a  
Double Mutant of a *Bacillus Subtilis*  
Esterase

**Four of the best:** Reaction of dimethylzinc with isopropyl carbodiimide at elevated temperature occurs with C–C bond formation and subsequent formation of polynuclear zinc amidinate complexes (see picture for tetranuclear complex, whose ligand is formed by the coupling of four carbodiimide ligands). Such a reaction is without precedent in amidinate chemistry.



## Zinc Amidinate Complexes

M. Münch, U. Flörke, M. Bolte, S. Schulz,\*  
D. Gudat 1512–1514

Unexpected C–C Bond Formation and  
Synthesis of Tetranuclear Zinc  
Carbodiimide Clusters from the Reaction  
of  $\text{ZnMe}_2$  and  $i\text{PrN}=\text{C}=\text{NiPr}$



## DNA Methylation

D. Kuch, L. Schermelleh, S. Manetto,  
H. Leonhardt, T. Carell\* 1515–1518

Synthesis of DNA Dumbbell Based  
Inhibitors for the Human DNA  
Methyltransferase Dnmt1

**Dumbbells that block:** Dnmt1 is a crucial enzyme in maintaining the methylation pattern of genes and as such is a critical element of the epigenetic programming process. DNA dumbbell constructs have been developed that inhibit Dnmt1 and

have potential in the regulation of DNA methylation patterns in cells (see scheme; SAM = S-adenosylmethionine, Fl = Cy3 fluorescence label,  $\text{C}^N$  = 5-azadC, C-Me = 5-methylidC).



Supporting information is available on the WWW (see article for access details).



A video clip is available as Supporting Information on the WWW (see article for access details).

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