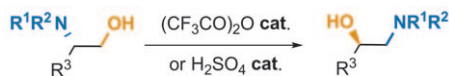


## CONCEPTS

### Enantioselective Rearrangement

T.-X. Métro, D. Gomez Pardo,\*  
J. Cossy\* ..... 1064–1070

#### Highly Enantioselective Synthesis of Linear $\beta$ -Amino Alcohols



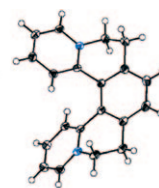
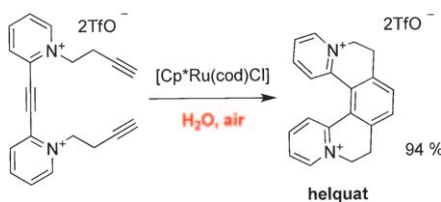
**Rearranging amino alcohols:** Treatment of  $\beta$ -amino alcohols derived from  $\alpha$ -amino acids with a catalytic amount of  $(\text{CF}_3\text{CO})_2\text{O}$  or  $\text{H}_2\text{SO}_4$  leads to the

formation of rearranged  $\beta$ -amino alcohols with good yield and high enantioselectivity (see scheme).

## COMMUNICATIONS

### Azoniahelicene Derivatives

L. Adriaenssens, L. Severa, T. Šalová,  
I. Čisarová, R. Pohl, D. Šaman,  
S. V. Rocha, N. S. Finney, L. Pospíšil,  
P. Slavíček, F. Teplý\* ..... 1072–1076



#### Helquats: A Facile, Modular, Scalable Route to Novel Helical Dications

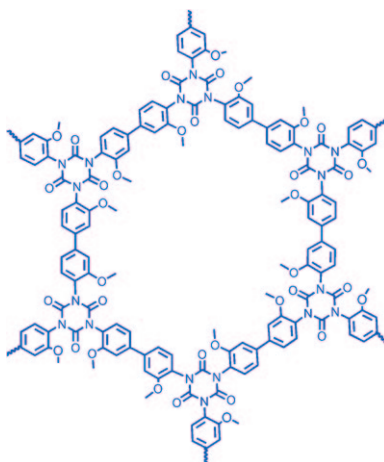
**As easy as one, two, three:** Relying on a facile  $[2+2+2]$ -cycloisomerization strategy, we have developed a robust three-step synthetic entry into a novel family of helical extended diquats (helquats). The key metal-catalyzed step

proceeds in water under aerobic conditions to produce a water-soluble, blue fluorophore (picture; TfO = triflate). The electrochemical manifold of the parent helquat features two reversible one-electron reduction steps.

### Microporous Polymers

Y. Zhang,\* S. N. Riduan,  
J. Y. Ying\* ..... 1077–1081

#### Microporous Polyisocyanurate and Its Application in Heterogeneous Catalysis

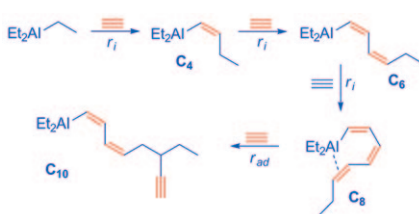


**Support your catalyst:** A new method has been developed to synthesize microporous polyisocyanurate (see figure). This polymer possesses urea-type rigid functional framework, high surface area, and permanent microporous structure. It is successfully applied as a support for iron oxide, and demonstrates excellent activity, selectivity and recyclability in the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide in water.

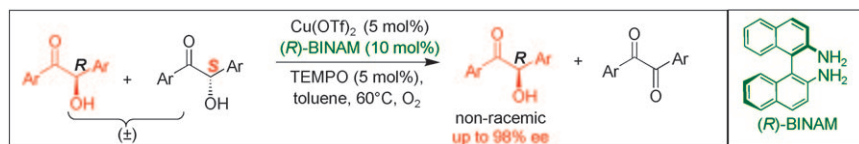
### Catalysis

S. Karpińiec, D. McGuinness,\* J. Patel,  
N. Davies ..... 1082–1085

#### Revisiting the Aufbau Reaction with Acetylene: Growth at Aluminium Producing a Unique Oligomer Distribution



**Growth at both ends:** The reaction of acetylene with triethylaluminium has been revisited (see scheme), and unlike the Aufbau reaction with ethylene, growth at aluminium produces branched acetylene oligomers. This hitherto unseen process seems to occur via both conventional migratory insertion and a second mode of acetylene addition across unsaturation in the growing chain, thus giving rise to a peculiar oligomer distribution.



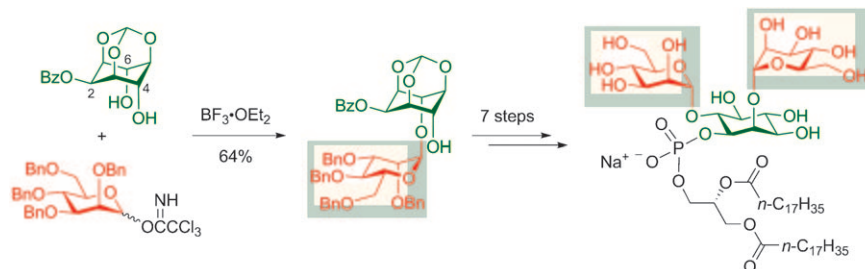
**GO for it!** An enantiopure galactose oxidase (GO) enzyme model has been synthesized from readily available (*R*)-binam and Cu(OTf)<sub>2</sub> (see scheme; TEMPO = 2,2,6,6-tetramethyl-piperidin-1-oxyl), and has been effectively used as an efficient chiral catalyst for

the oxidative kinetic resolution of secondary alcohols. This is the first chiral copper-catalyzed oxidative kinetic resolution of racemic benzoin and the simplest method for the synthesis of highly important enantiomerically enriched benzoin.

## Aerobic Oxidation

S. K. Alamsetti, S. Mannam, P. Mutupandi, G. Sekar\* ... 1086–1090

**Galactose Oxidase Model: Biomimetic Enantiomer-Differentiating Oxidation of Alcohols by a Chiral Copper Complex**



**A concise synthesis** of phosphatidylinositol dimannoside (PIM<sub>2</sub>) from commercially available *myo*-inositol 1,3,5-orthoformate via a highly regioselective and stereoselective 6-*O*-

mannosylation of the *myo*-inositol-derived *meso*-4,6-diol as a key step was carried out in 9 steps (see scheme) and in 13 % overall yield.

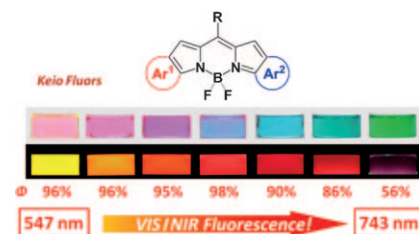
## Carbohydrates

P. S. Patil, S.-C. Hung\* ..... 1091–1094

**Total Synthesis of Phosphatidylinositol Dimannoside: A Cell-Envelope Component of *Mycobacterium tuberculosis***

# FULL PAPERS

**New fluorescent dyes—any color you want:** A new series of bright and long-wavelength fluorescent dyes (Keio Fluors), with sophisticated optical performance, have been created. Our “tailor-made” strategy allowed easy and fine tuning of emission peaks over a wide spectral range from the visible to the near-infrared region.

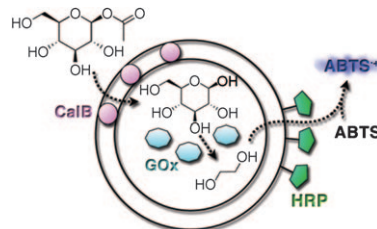


## Dyes/Pigments

K. Umezawa, A. Matsui, Y. Nakamura, D. Citterio, K. Suzuki\* ..... 1096–1106

**Bright, Color-Tunable Fluorescent Dyes in the Vis/NIR Region: Establishment of New “Tailor-Made” Multi-color Fluorophores Based on Boron-dipyrromethene**

**An enzyme triad:** A porous polymer-some was equipped with three different enzymes at three spatially separate locations: *Candida antarctica* lipase B (CalB) in its lumen, glucose oxidase (GOx) in its bilayer membrane and horseradish peroxidase (HRP) conjugated to its surface (see figure; ABTS = 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)). The encapsulation efficiency of the enzymes was determined, and their activity as part of a three-enzyme cascade reaction was investigated.



## Polymersomes

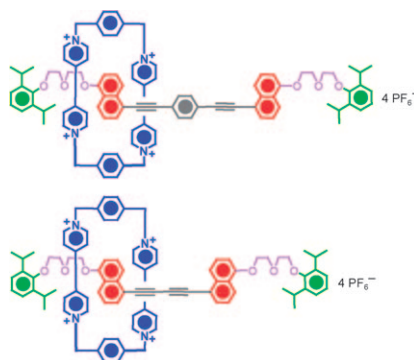
S. F. M. van Dongen, M. Nallani, J. J. L. M. Cornelissen, R. J. M. Nolte, J. C. M. van Hest\* ..... 1107–1114

**A Three-Enzyme Cascade Reaction through Positional Assembly of Enzymes in a Polymersome Nano-reactor**

## Rotaxanes

I. Yoon, D. Benítez, Y.-L. Zhao,  
O. Š. Miljanić, S.-Y. Kim,  
E. Tkatchouk, K. C.-F. Leung,  
S. I. Khan, W. A. Goddard, III,  
J. F. Stoddart\* ..... 1115–1122

### Functionally Rigid and Degenerate Molecular Shuttles

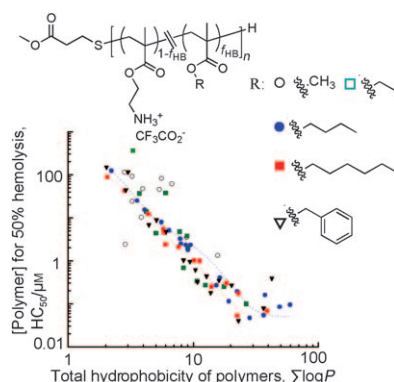


**Rigidity makes for faster molecular shuttles:** In the rigid donor–acceptor degenerate [2]rotaxanes, the tetra-cationic cyclophane shuttles back and forth between the two monosubstituted naphthalene stations via the rigid linker in the dumbbell-shaped components. Introducing rigidity has led to faster shuttling processes, corresponding to lower energy barriers than those formed in more flexible donor–acceptor rotaxanes.

## Polymers

K. Kuroda,\* G. A. Caputo,\*  
W. F. DeGrado ..... 1123–1133

### The Role of Hydrophobicity in the Antimicrobial and Hemolytic Activities of Polymethacrylate Derivatives

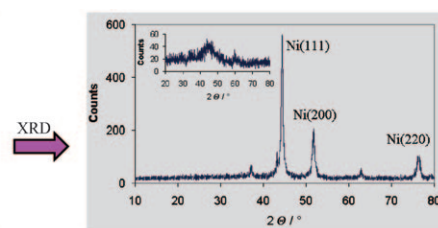
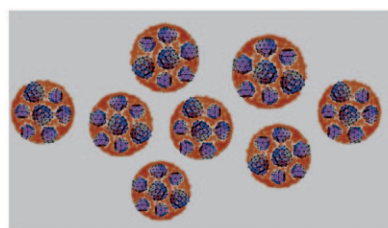


**The antimicrobial and hemolytic activities** of cationic polymethacrylate derivatives are driven by the total hydrophobicity of polymers (see picture). Polymer hydrophobicity results in collapse of the polymer chain in solution, causing a turnover of hemolytic activity. This effect also limits the efficacy and selectivity of synthetic polymers towards bacteria relative to erythrocytes.

## Nanomaterials

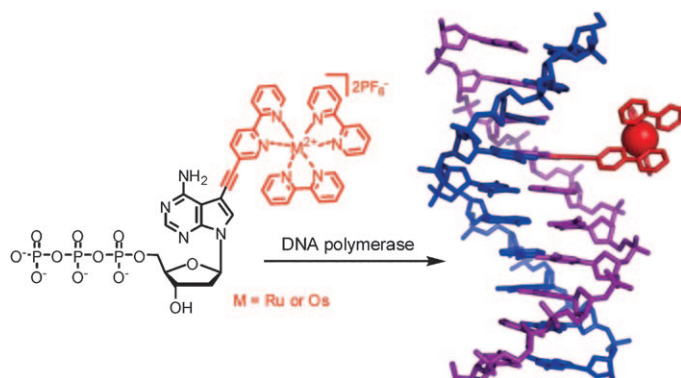
J. Geng,\* D. A. Jefferson,  
B. F. G. Johnson\* ..... 1134–1143

### Exploring the Structural Complexities of Metal–Metalloid Nanoparticles: The Case of Ni–B as Catalyst



**Complex nanostructure!** A systematic investigation on the catalytic Ni–B nanoparticles (see figure) revealed that the material has a highly unusual ultra-

fine nanostructure that offers an explanation as to why the catalyst is highly active in hydrogenation and dehydrogenation reactions.



**Metal-labeled DNA:** DNA-bearing  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Os}(\text{bpy})_3]^{2+}$  complexes have been constructed by polymerase incorporation of the corresponding base-modified nucleoside triphosphates (see figure). The Ru-modi-

fied DNA was luminescent, while the Os complexes could be detected by electrochemistry. A complete four-color redox labeling of DNA has been developed and used for mini-sequencing.

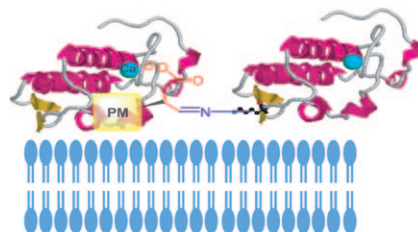
## Metal-Labeled DNA

*M. Vrábel, P. Horáková, H. Pivoňková, L. Kalachova, H. Černocká, H. Čahová, R. Pohl, P. Šebest, L. Havran, M. Hocek,\* M. Fojta\** ..... 1144–1154

**Base-Modified DNA Labeled by  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Os}(\text{bpy})_3]^{2+}$  Complexes: Construction by Polymerase Incorporation of Modified Nucleoside Triphosphates, Electrochemical and Luminescent Properties, and Applications**



**Two is better than one?** The amphiphilic petrosaspongiolide M (PM), a  $\gamma$ -hydroxybutenolide marine terpenoid, specifically inhibits human group IIA secretory phospholipase  $\text{A}_2$  (sPLA $_2$ -IIA). PM selectively reacts with the Lys67 residue located near the enzyme–membrane interfacial binding surface. Covalent modification of PM generates a PLA $_2$ -bound phospholipid-like molecule that can target the active site of another sPLA $_2$ -IIA unit (see picture). This unusual binding mode would lead to a potent dual inhibition.



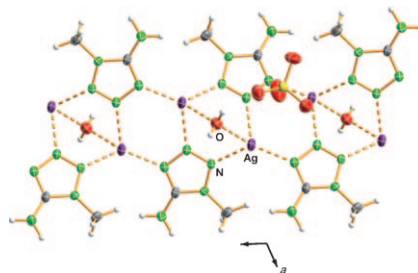
## Enzyme Inhibition

*M. C. Monti, A. Casapullo,\* C. N. Cavasotto, A. Tosco, F. Dal Piaz, A. Ziemys, L. Margarucci, R. Riccio\** ..... 1155–1163

**The Binding Mode of Petrosaspongiolide M to the Human Group IIA Phospholipase  $\text{A}_2$ : Exploring the Role of Covalent and Noncovalent Interactions in the Inhibition Process**



**Full of energy!** A new family of silver complexes with heterocyclic ligands and perchlorate or nitrate anions with interesting structural details, such as a heteronorborane skeleton (see picture), are presented. The energetic properties of these materials are compared with those of the proton analogues, revealing increased sensitivities and good thermal stabilities.



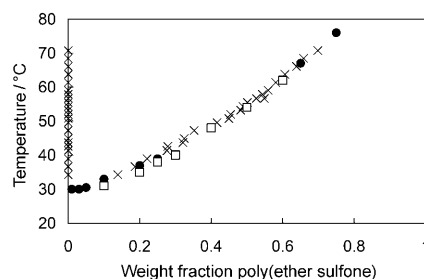
## Energetic Materials

*K. Karaghiosoff, T. M. Klapötke,\* C. Miró Sabaté* ..... 1164–1176

**Energetic Silver Salts with 5-Aminotetrazole Ligands**



**And relax!** A new and elegant method for studying the phase behavior of liquid (polymer) blend systems by using  $T_2$  NMR relaxometry is reported (see figure for the coexistence curve of P(EO-*ran*-PO)/PES as constructed by a stepwise isothermal  $T_2$  NMR relaxometry experiment ( $\times$ ), starting from four blends with well-chosen compositions).



## NMR Relaxometry

*L. Van Lokeren, N.-A. Gotzen, R. Pieters, G. Van Assche,\* M. Biesemans, R. Willem, B. Van Mele\** ..... 1177–1185

**Phase Behavior in Blends of Ethylene Oxide–Propylene Oxide Copolymer and Poly(ether sulfone) Studied by Modulated-Temperature DSC and NMR Relaxometry**

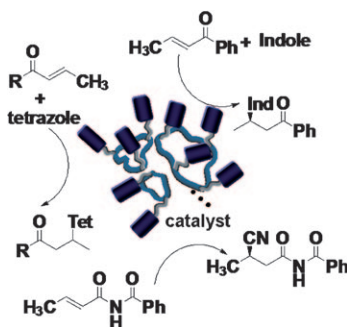


## Asymmetric Catalysis

N. Madhavan, T. Takatani,  
C. D. Sherrill, M. Weck\* .... 1186–1194



### Macrocyclic Cyclooctene-Supported AlCl<sub>3</sub>-Salen Catalysts for Conjugated Addition Reactions: Effect of Linker and Support Structure on Catalysis



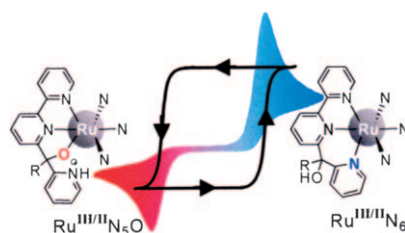
**Lending support!** AlCl<sub>3</sub>-salen (salen = *N,N'*-bis(salicylidene)ethylene-diamine dianion) catalysts attached to macrocyclic oligomeric cyclooctene supports through linkers of varying length and flexibility demonstrate the importance of support architecture on catalytic activity for bimetallic as well as monometallic reactions (see scheme).

## Molecular Switches

O. Johansson,\* L. O. Johannissen,  
R. Lomoth\* ..... 1195–1204



### Bistable Molecular Switches Based on Linkage Isomerization in Ruthenium Polypyridyl Complexes with a Ligand-Bound Ambidentate Motif



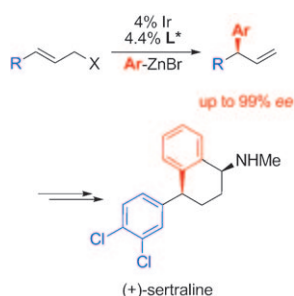
**Reversible switching** of a ligand-bound ambidentate motif between N and O coordination in the Ru<sup>II</sup> and Ru<sup>III</sup> state, respectively, is shown by Ru complexes with an ambidentate ligand and a substituted terpyridine ligand (Y-tpy). The potential difference of the Ru<sup>III/II</sup> couple of about 0.5 V between the isomers results in a bistable electrochemical response of these molecular switches (see scheme; only N donors of tpy ligand shown).

## Asymmetric Synthesis

D. Polet, X. Rathgeb, C. A. Falcioni,  
J.-B. Langlois, S. E. Hajjaji,  
A. Alexakis\* ..... 1205–1216



### Enantioselective Iridium-Catalyzed Allylic Arylation

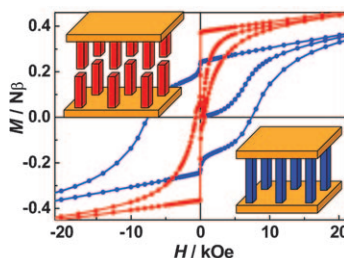


**Instant transfer:** This full paper describes the development of a catalytic system that allows for high enantioselectivities in the allylic arylation of nonsymmetrical electrophiles and was applied towards the formal synthesis of (+)-sertraline (see scheme). The emphasis of this research was placed on the scope, the limitations, the synthetic applications, and the mechanistic aspects of this system.

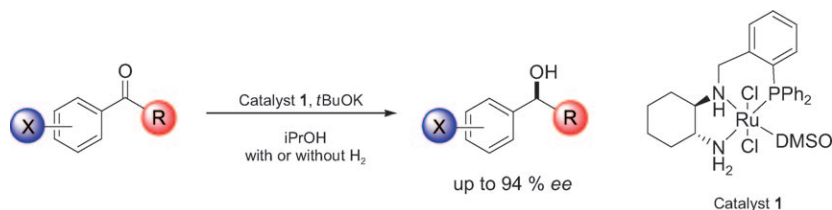
## Molecular Magnets

E.-Q. Gao,\* P.-P. Liu, Y.-Q. Wang,  
Q. Yue, Q.-L. Wang ..... 1217–1226

### Complex Long-Range Magnetic Ordering Behaviors in Anisotropic Cobalt(II)-Azide Multilayer Systems



**Ordered about:** Cobalt(II)-azide layers are isolated or cross-linked by organic ligands to give 2D or 3D molecular magnets that exhibit unusual long-range-ordering properties that combine spin canting, metamagnetism, and exotic hysteresis (see figure). The two materials contain almost identical layers, which allow us to determine the influence of the inter-layer separation on the magnetic properties.



**Making some room:** A new class of ruthenium catalyst derived from a tridentate  $P^N^N$  ligand (see picture) has been shown to be active in the enantioselective hydrogenation and

transfer hydrogenation of bulky, deactivated ketones—substrates that are problematic using most Noyori-type catalysts.

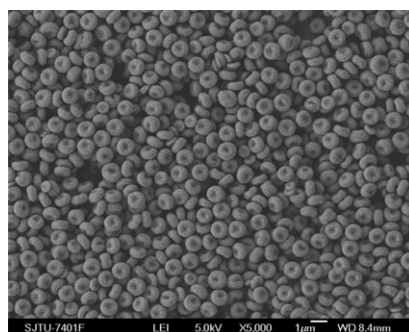
## Homogeneous Catalysis

*M. B. Díaz-Valenzuela, S. D. Phillips, M. B. France, M. E. Gunn, M. L. Clarke\* ..... 1227–1232*

**Enantioselective Hydrogenation and Transfer Hydrogenation of Bulky Ketones Catalysed by a Ruthenium Complex of a Chiral Tridentate Ligand**



**Lanthanide orthovanadate:** Nearly monodisperse  $YVO_4$  architectures with persimmon-like (shown here), cube-like and nanoparticle shapes have been synthesised on a large scale by a complexing-agent-assisted solution route. The shape and size of these as-prepared architectures can be tuned effectively by controlling the reaction conditions.



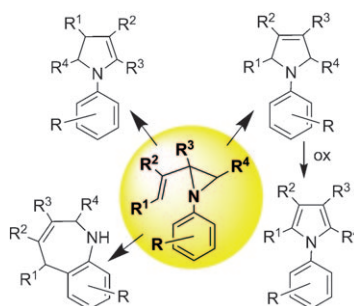
## Nanostructures

*L. Qian, J. Zhu, Z. Chen, Y. Gui, Q. Gong, Y. Yuan, J. Zai, X. Qian\* ..... 1233–1240*

**Self-Assembled Heavy Lanthanide Orthovanadate Architecture with Controlled Dimensionality and Morphology**



**Rearrange your chemistry!** Herein we report the one-pot synthesis of several N-heterocyclic compounds by rearrangement reactions of N-aryl-2-vinylaziridines (see scheme). To rationalize the experimental results reported in this paper, a theoretical study was also performed.



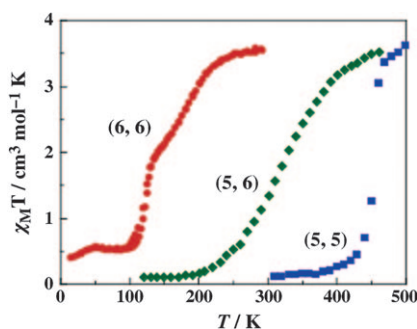
## Nitrogen Heterocycles

*S. Fantauzzi, E. Gallo,\* A. Caselli, C. Piangiolino, F. Ragaini, N. Re, S. Cenini ..... 1241–1251*

**Rearrangement of N-Aryl-2-Vinylaziridines to Benzoazepines and Dihydropyrroles: A Synthetic and Theoretical Study**



**Strain effects on spin-transition temperature:** Structural and magnetic studies (see figure) of a family of iron(II) complexes show that the spin-crossover temperature depends on the strain effects from the size of chelate rings. The effect of the successive reduction in size from a six- to five-membered chelate ring independently on the counterion nature leads to a rise in transition temperature.



## Iron Complexes

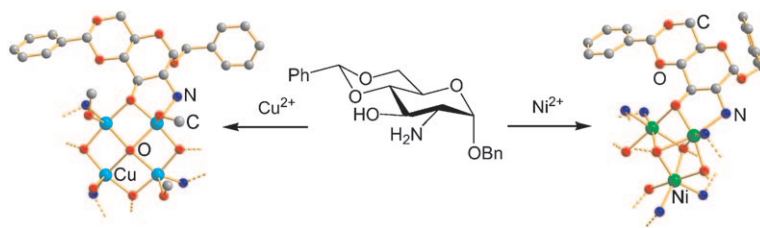
*G. S. Matouzenko,\* S. A. Borshch, E. Jeanneau, M. B. Bushuev ..... 1252–1260*

**Spin Crossover in a Family of Iron(II) Complexes with Hexadentate ligands: Ligand Strain as a Factor Determining the Transition Temperature**

## Carbohydrate Ligands

A. Burkhardt, E. T. Spielberg,  
S. Simon, H. Görls, A. Buchholz,  
W. Plass\* ..... 1261–1271

**Hydrogen Bonds as Structural Directive towards Unusual Polynuclear Complexes: Synthesis, Structure, and Magnetic Properties of Copper(II) and Nickel(II) Complexes with a 2-Amino-glucose Ligand**




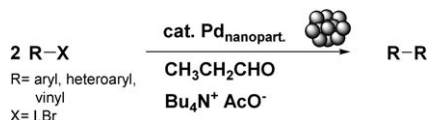
**Sweet control:** Depending on their functionalization aminoglucose ligands were found to support different structural motifs. This leads to an unex-

pected  $\mu_4$ -OH-bridged tetranuclear copper as well as a trinuclear nickel complex with a ferromagnetic ground state (see figure).

## Biaryl Synthesis


V. Calò, A. Nacci,\* A. Monopoli,  
P. Cotugno ..... 1272–1279


 **Palladium-Nanoparticle-Catalysed Ullmann Reactions in Ionic Liquids with Aldehydes as the Reductants: Scope and Mechanism**




**An unusual reduction:** A new method for synthesising symmetrical biaryls has been developed by making use of Pd colloids as the catalyst, an aldehyde as the reducing agent and an ionic liquid as the reaction medium (see scheme). Aryl bromides and iodides are activated without the use of special additives or ligands, under relatively mild conditions (reaction temperatures ranging from 40 to 90°C).

\* Author to whom correspondence should be addressed

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