**Cover**

The iron-tantalum bridging alkylidene $(\text{Me}_2\text{SiCH}_2)[\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]\text{Ta}(\text{CHSiMe}_2)(i\text{-Pr}_2\text{-tacn})\text{FeCl}$ (phenyl $i\text{-Pr}$ groups omitted for clarity). The search for new classes of supporting ligands in transition metal chemistry has resulted in recent work involving the anionic triazacyclononane (tacn) group, which has been shown to function as an unusual 6-electron donor ligand in the first examples of early transition metal complexes (pp. 1025–1033)

contents

FOCUS ARTICLE

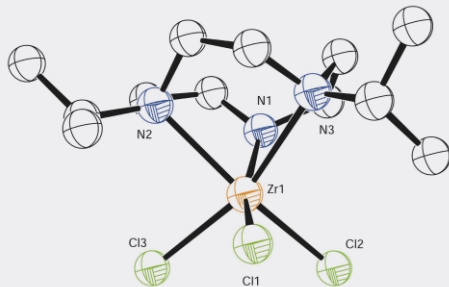
1021

**Diamond will shine brightly for chemistry**

Diamond, the new generation synchrotron light source set to open at the Rutherford Appleton Laboratory in 2007, should push back the boundaries of what chemists can achieve in many research areas.

FEATURE ARTICLE

1025

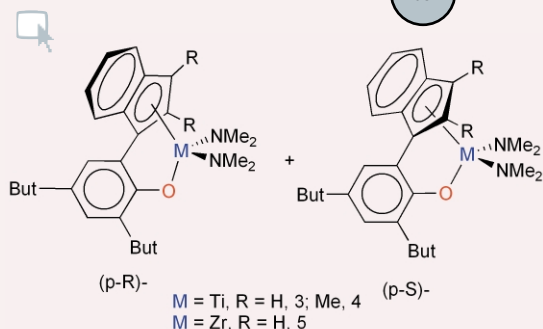
**Anionic triazacyclononanes: new supporting ligands in main group and transition metal organometallic chemistry**

Joseph A. R. Schmidt, Garth R. Giesbrecht, Chunming Cui and John Arnold*

A significant fraction of modern organometallic chemistry is made possible by the presence of spectator ligands that provide stability and reactivity to their metal complexes. As part of an ever-growing arsenal of supporting ligands, recent advances in the chemistry of anionic triazacyclononanes have led to a burgeoning series of new complexes, whose chemistry is described here.

COMMUNICATIONS

1034

**Facile resolution of constrained geometry indenyl-phenoxide ligation**

Luke E. Turner, Matthew G. Thorn, Phillip E. Fanwick and Ian P. Rothwell*

The 2-(inden-3-yl)phenoxide ligand can be resolved at both tetrahedral and octahedral Group 4 metal centers using chiral binaphthoxide ligands.

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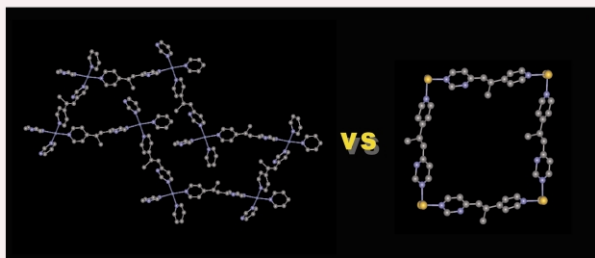
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Coordination polymers based on square planar Co(II) node and linear spacer: solvent-dependent pseudo-polymorphism and an unprecedented interpenetrating structure containing both 2D and 3D topological isomers

Dong Mok Shin, In Su Lee, Young Keun Chung* and Myoung Soo Lah

Reaction of $\text{Co}(\text{NCS})_2$ with 1-methyl-1'-(4-pyridyl)-2-(4-pyrimidyl)-ethylene (mppe) in different solvents yields two kinds of novel coordination polymer structures of $[\text{Co}(\text{mppe})_2(\text{NCS})_2]_n$.

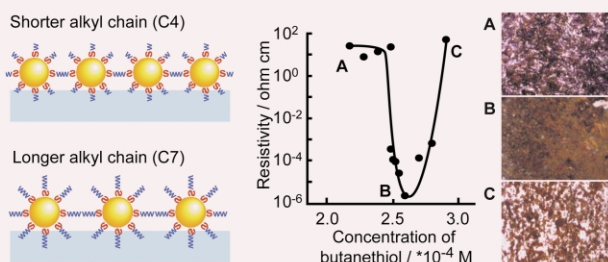


1038

Electrical property and water repellency of a networked monolayer film prepared from Au nanoparticles

Hiroshi Shiigi, Yojiro Yamamoto, Hidetaka Yakabe, Shiho Tokonami and Tsutomu Nagaoka*

The alkyl chain length and concentration of thiol used as a binder was found to dramatically change the conductivity and hydrophobicity of the Au nanoparticle monolayer on polystyrene (PS).

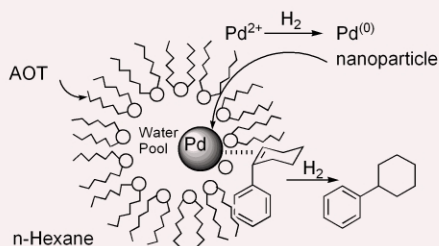


1040

Dispersing palladium nanoparticles using a water-in-oil microemulsion—homogenization of heterogeneous catalysis

Byunghoon Yoon, Hakwon Kim and Chien M. Wai*

Palladium nanoparticles stabilized and dispersed in a water-in-hexane microemulsion are effective catalysts for hydrogenation of olefins.

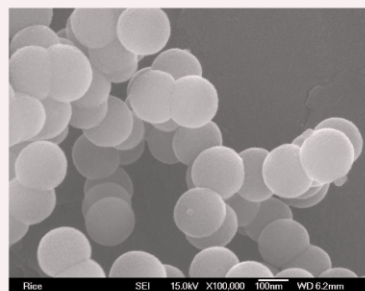


1042

Silica coated fullerenols: seeded growth of silica spheres under acidic conditions

Elizabeth A. Whitsitt and Andrew R. Barron*

Liquid phase deposition of silica in the presence of fullereneol, $\text{C}_{60}(\text{OH})_n$, results in the formation of uniform silica spheres in which the C_{60} is retained as the core of the silica spheres.

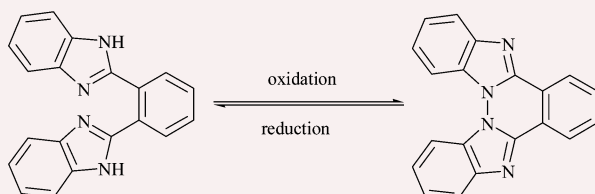


1044

Cyclodehydrogenation of di- and tetra(benzimidazol-2-yl)benzenes to give model heteroaromatic discotic systems

Weicheng Wu, Andrew C. Grimsdale and Klaus Müllen*

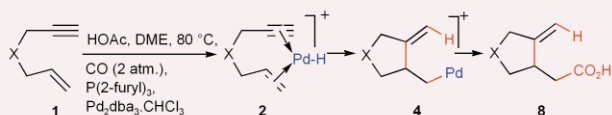
Di- and tetra(benzimidazol-2-yl)benzenes upon oxidation undergo cyclodehydrogenation with formation of N–N bonds to form planarized polycyclic compounds which are models for the cores of heteroatom-containing discotic materials, and which can be readily reduced back to the original compounds, thus demonstrating a molecular redox switch.



1046

Palladium catalysed cyclisation–carbonylation of enynes to give cyclic γ,δ -unsaturated acids

Varinder K. Aggarwal,* Mike Butters and Paul W. Davies

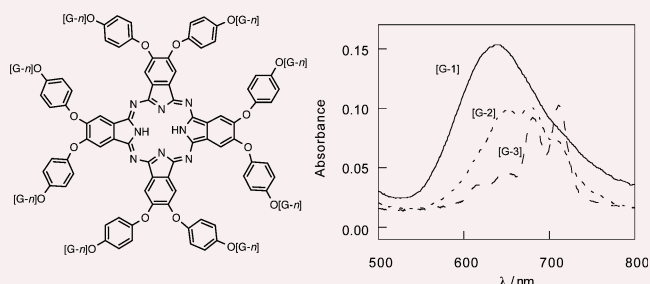


In the presence of acetic acid, trifurylphosphine and CO (2 atm), palladium catalyses the conversion of a range of enynes to cyclic δ,γ -unsaturated carboxylic acids in good yield.

1048

Non-aggregating octasubstituted dendritic phthalocyanines

Casey A. Kernag and Dominic V. McGrath*

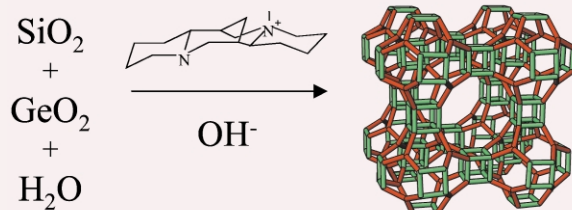


Eight poly(aryl) ether dendritic wedges attached to the periphery of a phthalocyanine significantly decreases self-association of these chromophores in solution and the condensed state.

1050

Synthesis of ITQ-21 in OH^- media

A. Corma,* M. J. Díaz-Cabañas and F. Rey

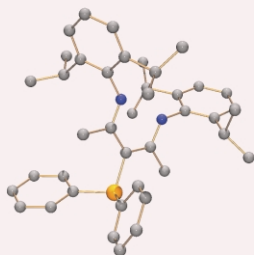
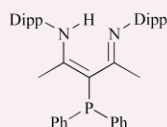


ITQ-21 has been synthesized from F^- free gels. The introduction of stoichiometric amounts of NH_4F leads to an increase in the nucleation and crystallization rate.

1052

Inhibited chelation in the new γ -phosphino- β -diketiminate to give phosphine \rightarrow arsine coordination

Paul J. Ragogna, Neil Burford,* Mark D'eon and R. McDonald

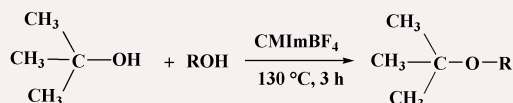


A γ -diphenylphosphino- β -diketimine has been synthesised and the ^{31}P NMR handle allows for *in situ* analysis of reaction mixtures revealing unprecedented reactivity with AsCl_3 to give a novel phosphinoarsine intramolecular coordination complex.

1054

The first non-acid catalytic synthesis of *tert*-butyl ether from *tert*-butyl alcohol using ionic liquid as dehydrator

Feng Shi, Hai Xiong, Yanlong Gu, Shu Guo and Youquan Deng*



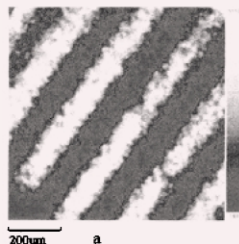
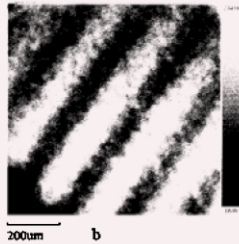
tert-butyl ethers were synthesized for the first time over a non-acid ionic liquid as catalyst and dehydrator with 93% of conversion and 97% of selectivity under mild reaction conditions.

1056

Micropatterns constructed from Au nanoparticles

Conghua Lu, Nianzu Wu, Xiaoming Jiao, Chuanqiu Luo and Weixiao Cao*

Covalently linked Au-NPs micropatterns were fabricated from the self-assembly film composed of 4-mercaptophenol-capped Au-NPs and photoactive polymer NDR by selective exposure to UV light and subsequent development in SDS aqueous solution. The resultant Au-NPs micropatterns were characterized by AFM and XPS.

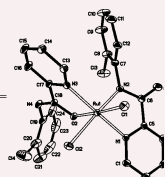
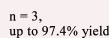
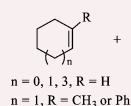
(a): Au 4f_{7/2}(b): Si2p_{3/2}

1058

Highly efficient epoxidation of cyclic alkenes catalyzed by ruthenium complex

Jian Ying Qi, Li Qin Qiu, Kim Hung Lam, Chiu Wing Yip, Zhong Yuan Zhou and Albert S. C. Chan*

The epoxidation of cyclic alkenes with molecular oxygen was efficiently completed in excellent epoxide yield using a novel ruthenium complex as catalyst under mild reaction conditions.

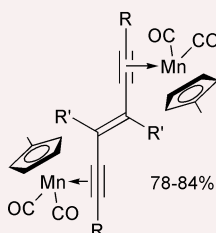
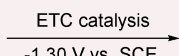
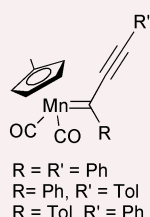


1060

Electrocatalytic dimerisation of non-heteroatom-substituted manganese alkynylcarbene complexes

Yannick Ortin, Alix Sournia-Saquet, Noël Lugan* and René Mathieu

Upon controlled potential electrolysis, non-heteroatom-substituted manganese alkynylcarbene complexes undergo an electrocatalytic dimerisation by coupling of the remote carbon atoms.

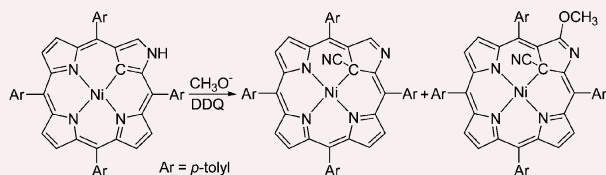


1062

Inner C-cyanide addition and nucleophilic addition to Ni(II) N-confused porphyrins

Ziwei Xiao, Brian O. Patrick and David Dolphin*

Inner C-cyanide addition and subsequent addition of a methoxy group were observed in the reactions of Ni(II) N-confused tetra(*p*-tolyl)porphyrin with sodium methoxide and DDQ.

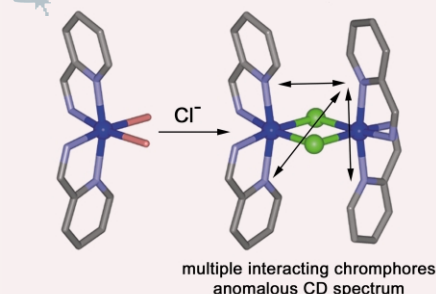


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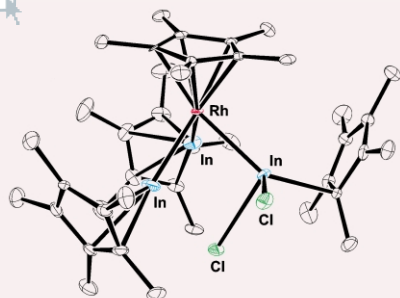
Stereoselective formation of dinuclear complexes with anomalous CD spectra

Shane G. Telfer,* Reiko Kuroda* and Tomohiro Sato

A novel chiral tetradentate Schiff base ligand forms dinuclear $[\text{M}_2\text{L}_2\text{Cl}_2]^{2+}$ complexes with high diastereoselectivity. The complexes exhibit anomalous CD spectra due to the interaction of chromophores located on different metal centres.



1066

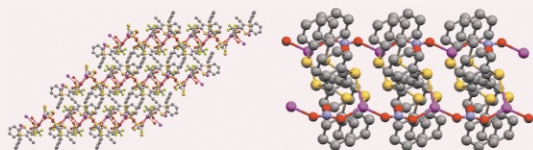


Insertion of organoindium carbenoids into rhodium halide bonds: revisiting a classic type of transition metal–group 13 metal bond formation

Tobias Steinke, Christian Gemel, Mirza Cokoja, Manuela Winter and Roland A. Fischer*

Insertion of InCp^* (Cp^* = pentamethylcyclopentadienyl) and $\text{InC}(\text{SiMe}_3)_3$ into the $\text{Rh}-\text{Cl}$ bonds of $[\{\text{RhCp}^*\text{Cl}_2\}_2]$ yields the new complexes $[\text{Cp}^*\text{Rh}(\text{InCp}^*)_3(\text{Cl})_2]$ and $[\text{Cp}^*\text{Rh}\{\text{InC}(\text{SiMe}_3)_3\}_3(\text{Cl})_2]$, exhibiting novel cage-like intermetallic complexes with $\text{In}-\text{Cl}-\text{In}$ bridges.

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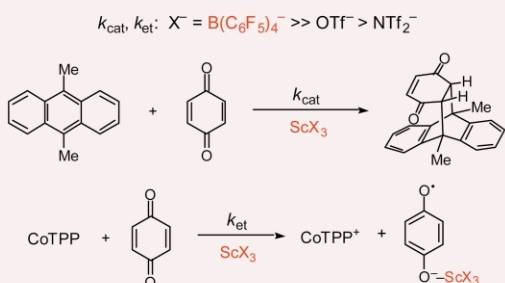


Photoluminescent supramolecular networks from metal-mediated assembly of polythia conjugated dieneynes

Yuan-Te Fu, Vincent M. Lynch and Richard J. Lagow*

A new class of photofunctional polythia conjugated dieneynes has been synthesized and utilized as a building block to construct fluorescent supramolecular networks based on metal-directed self-organization.

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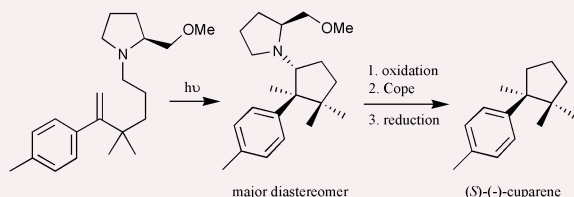


Remarkable effects of counter ions on scandium ion-promoted electron transfer reactions

Junpei Yuasa, Tomoyoshi Suenobu, Kei Ohkubo and Shunichi Fukuzumi*

Scandium ion-promoted electron transfer and scandium ion-catalyzed Diels–Alder reactions of *p*-benzoquinone are remarkably accelerated when tetrakis(pentafluorophenyl)borate anion is used instead of trifluoromethanesulfonate anion as the counter anion of scandium ion.

1072

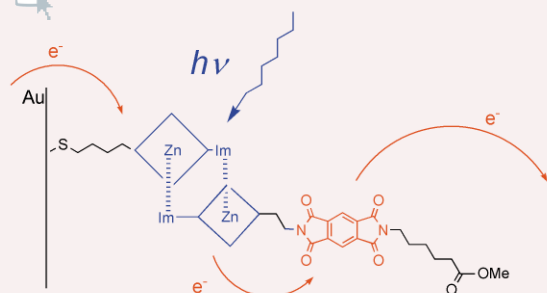


Photomediated asymmetric synthesis of (–)-cuparene

Richard S. Grainger* and Aslam Patel

Generation of a benzylic quaternary stereocentre *via* the photomediated cyclisation of a chiral α -(aminobutyl)styrene followed by a microwave-assisted Cope elimination has led to a total synthesis of the sesquiterpene (–)-cuparene.

1074



Porphyrin hetero-dimer as charge separating system for photocurrent generation

Akihiro Nomoto, Hiroaki Mitsuoka, Hidekane Ozeki and Yoshiaki Kobuke*

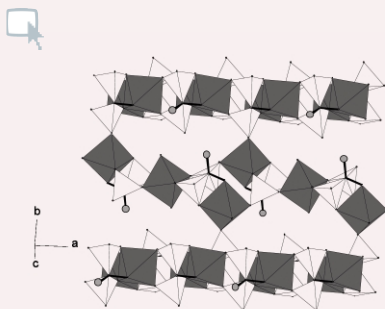
The porphyrin hetero-dimer was formed easily onto an electrode by a supramolecular method, and effective charge separation in the non-covalent porphyrin hetero-dimer contributed to improve the photocurrent generation.

1076

A two-step field-induced magnetic transition in a novel layered cobalt diphosphonate

Ping Yin, Song Gao, Li-Min Zheng,* Zheming Wang and Xin-Quan Xin

A novel layered compound $\text{Na}_6\text{Co}_7(\text{hedp})_2(\text{hedpH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ (hedp = 1-hydroxyethylidenediphosphonate) is reported which shows two-step magnetic transitions with the critical fields of *ca.* 6.5 kOe and 30 kOe, respectively, at 1.8 K.

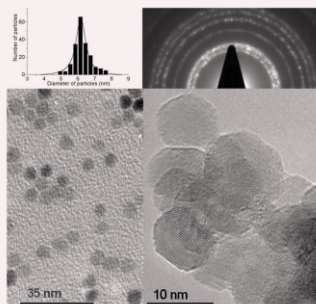


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Preparation of ZnO nanocrystals via ultrasonic irradiation

Dong Qian, J. Z. Jiang* and Poul Lenvig Hansen

A simple and rapid process has been developed for the preparation of narrow size distribution nanometer-sized ZnO crystals *via* ultrasonic irradiation.

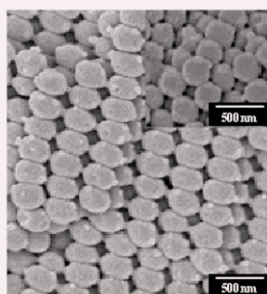


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Opal gel templated synthesis of oblate titania opal materials

Lijun Ji, Jianhua Rong and Zhenzhong Yang*

Oblate titania opal materials were made by a favorable sol/gel process of tetrabutyl titanate in the acid groups contained hydrogel opal templates under compression at ambient temperature.

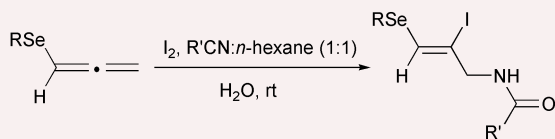


1082

Highly regio- and stereoselective four-component iodoamination of Se-substituted allenes. an efficient synthesis of *N*-(3-organoseleno-2-iodo-2(*Z*)-propenyl) acetamides

Shengming Ma,* Xueshi Hao and Xian Huang

An *E*-iodoamination of Se-substituted allenes with I_2 and $\text{R}'\text{CN}$ in the presence of H_2O was observed.

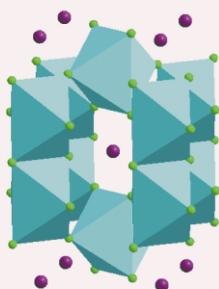


1084

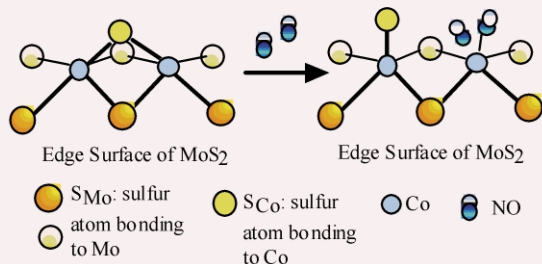
Optical and electrical properties of the wide gap, n-type semiconductors: ZnBi_2O_6 and MgBi_2O_6

Hiroshi Mizoguchi, Nattamai S. P. Bhuvanesh and Patrick M. Woodward*

Bi^{5+} trirutile oxides synthesized by hydrothermal process were found to be degenerate n-type semiconductors with optical bandgaps of 1.8 and 1.7 eV, for MgBi_2O_6 and ZnBi_2O_6 respectively. This combination of properties suggests that films of these materials may find application as transparent conductors.



1086

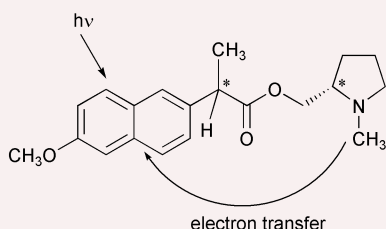


Fraction of the CoMoS phases accessible to NO in Co–Mo hydrodesulfurization catalysts

Yasuaki Okamoto,* Masatoshi Kawano and Takeshi Kubota

Nitric oxide molecules adsorb on 55% of the Co atoms on the edge sites of MoS₂ without oxidation, suggesting a Co pair structure for CoMoS phases.

1088



Stereoselective fluorescence quenching by photoinduced electron transfer in naphthalene-amine dyads

Uwe Pischel,* Sergio Abad and Miguel A. Miranda*

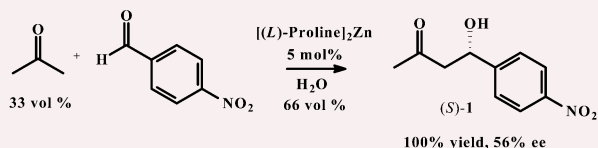
Chiral recognition is observed in the intramolecular electron transfer for diastereomeric naphthalene-amine dyads.

1090



Zn-Proline catalyzed direct aldol reaction in aqueous media

Tamis Darbre* and Miguel Machuqueiro



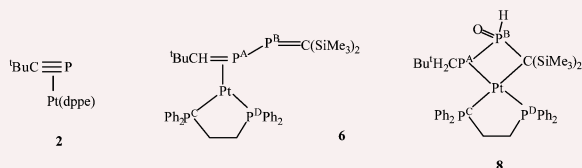
Zn complexes of proline, lysine and arginine are efficient catalysts for the direct aldol addition of p-nitrobenzaldehyde and acetone in aqueous medium, giving quantitative yields and enantiomeric excesses up to 56% with 5 mol% of the catalysts at room temperature.

1092



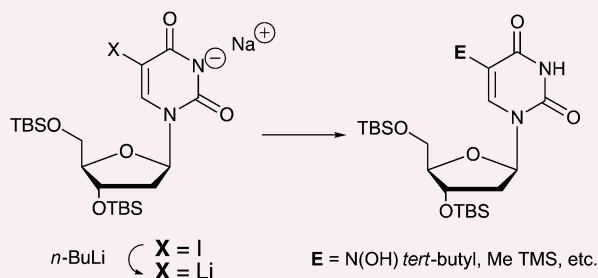
Synthesis of a η^2 -2,3-diphosphabutadiene complex of zerovalent platinum from the corresponding η^2 -phosphaalkyne complex

Maria Helena Araujo, Peter B. Hitchcock, John F. Nixon,* Uwe Kuehner and Othmar Stelzer



Hydrozirconation of the phosphaalkyne complex [Pt(dppe)(η^2 -^tBuCP)] **2** followed by treatment with the chlorophosphaalkene CIP=C(SiMe₃)₂ affords the η^2 -2,3-diphosphabutadiene complex [Pt(dppe)(η^2 -^tBuC(H)=PP=C(SiMe₃)₂)] **6** which adds water to produce [Pt(dppe)(^tBuCH₂P(O)HPC(SiMe₃)₂)] **8**.

1094



A simple and efficient method for synthesis of 5-substituted 2'-deoxyuridine nucleosides using metal–halogen exchange reaction of 5-iodo-2'-deoxyuridine sodium salt

Mariko Aso,* Toshiyuki Kaneko, Morihide Nakamura, Noboru Koga and Hiroshi Suemune*

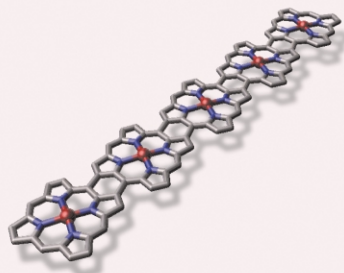
Treatment of the sodium salt of 2'-deoxy-3', 5'-bis-*O*-(*tert*-butyldimethylsilyl)-5-iodouridine with *n*-BuLi effected regioselective lithiation at the 5-position and the following reaction with various electrophiles afforded 5-substituted 2'-deoxyuridines.

1096

Synthesis of *meso*- β doubly linked porphyrin tapes

Akihiko Tsuda, Yasuyuki Nakamura and Atsuhiko Osuka*

Oxidation of 5,15-bis(3,5-di-*tert*-butylphenyl) Ni(II)-porphyrin **1b** with Sc(OTf)₃ and DDQ led to production of *meso*- β doubly linked Ni(II)-porphyrin tapes that have large π -electronic communications over the arrays.

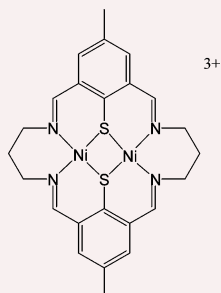


1098

Ni(III) vs. Ni(II)-thiyl radical: charge-delocalisation in a binuclear Ni(III)Ni(II)-dithiolate complex

Neil D. J. Branscombe, Andrew J. Atkins, Armando Marin-Becerra, Eric J. L. McInnes, Frank E. Mabbs, Jonathan McMaster and Martin Schröder*

Multi-frequency EPR spectroscopy on ⁶¹Ni-labelled samples of [Ni₂(L)]³⁺ confirms extensive charge-delocalisation between the Ni(III) centre and thiolate donors in the Ni(II)Ni(III) complex.

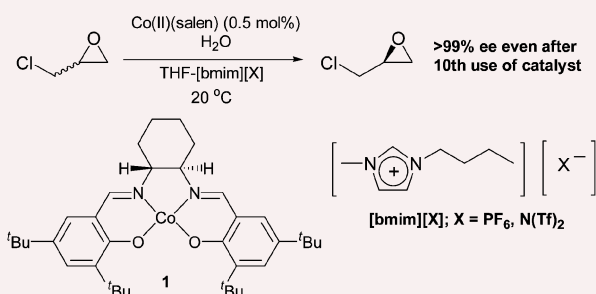


1100

Chiral Co(III)(salen)-catalysed hydrolytic kinetic resolution of racemic epoxides in ionic liquids

Chun Rim Oh, Dong Joon Choo, Woo Ho Shim, Dong Hoon Lee, Eun Joo Roh, Sang-gi Lee and Choong Eui Song*

In chiral Co(III)(salen)-catalysed hydrolytic kinetic resolution of racemic epoxides, in the presence of ionic liquids, **1** is oxidised without use of acetic acid to catalytically active Co(III)(salen) complex during reaction and this oxidation state is stabilised against reduction to Co(II) complex.

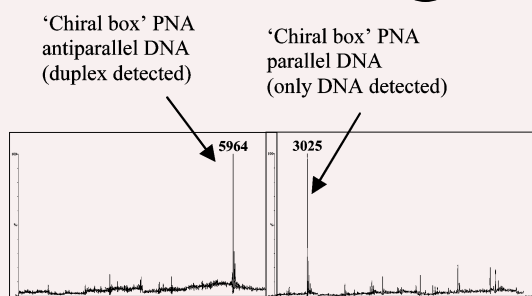


1102

Direction control in DNA binding of chiral D-lysine-based peptide nucleic acid (PNA) probed by electrospray mass spectrometry

Stefano Sforza,* Tullia Tedeschi, Roberto Corradini, Arnaldo Dossena and Rosangela Marchelli

ESI-MS has been used to demonstrate that a peptide nucleic acid (PNA) bearing three adjacent D-lysine-based residues in the middle of the strand ("chiral box") exerts perfect direction control (antiparallel vs. parallel DNA target) in DNA binding, in contrast with a standard achiral PNA.

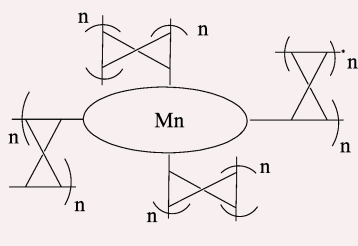


1104

Poly(9,9'-spirobifluorene-manganese porphyrin): a new catalytic material for oxidation of alkenes by iodobenzene diacetate and iodosylbenzene

Cyril Poriel, Yann Ferrand, Paul le Maux, Joëlle Raul-Berthelot* and Gerard Simonneaux*

Anodic oxidation of tetraspirobifluorene-manganese porphyrins lead to the coating of the working electrode by insoluble electroactive Poly(9,9'-spirobifluorene-manganese porphyrin) materials which are able to catalyse the heterogeneous epoxidation of styrene derivatives by iodobenzene diacetate and iodosylbenzene.



ADDITIONS AND CORRECTIONS

1106

Jennifer L. Beck, Rajesh Gupta,
Thitima Urathamakul, Nyree L.
Williamson, Margaret M. Sheil,
Janice R. Aldrich-Wright and
Stephen F. Ralph

Probing DNA selectivity of ruthenium metallointercalators using ESI mass spectrometry

1106

Hironao Sajiki, Takashi Ikawa,
Kazuyuki Hattori and Kosaku Hirota

A remarkable solvent effect toward the Pd/C-catalyzed cleavage of silyl ethers

1106

Akihiro Nomoto and Yoshiaki
Kobuke

Photocurrent generation system incorporated with antenna function

1107

Xiang Ouyang, Tsung-Yen Tsai,
Dong-Hwang Chen, Qi-Jie Huang,
Wu-Hsun Cheng and Abraham
Clearfield

Ab initio structure study from in-house powder diffraction of a novel ZnS(EN)_{0.5} structure with layered wurtzite ZnS fragment

1107

Hans Joachim Breunig, Mihaiela
Ghesner and Enno Lork

Synthesis of a stibindolyl anion from trimesitylantimony and potassium

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Dates, venues and contact details of forthcoming events.

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