

Cover (far left)
Catalytic cycle of oxidation of alcohols with aqueous hydrogen peroxide.

Inside cover (left)
Cations–organic interactions could be used to control excited state behavior of organic molecules.

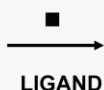
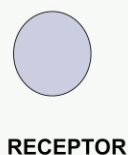
contents

FOCUS ARTICLE

1973

How can enzymes be so efficient?

Dudley H. Williams,* Elaine Stephens and Min Zhou



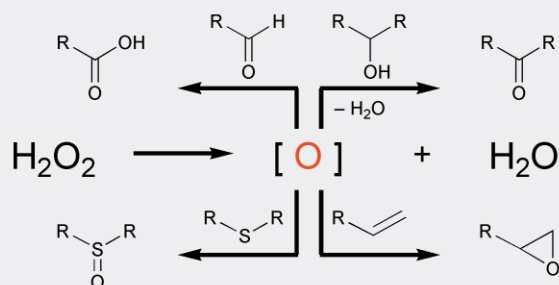
Ligands bind to receptors, and transition states to enzymes, with contraction of the structures of the proteins. Through this positively cooperative binding, ligand binding energy is promoted, or catalysis increased in efficiency.

FEATURE ARTICLE

1977

Green oxidation with aqueous hydrogen peroxide

Ryoji Noyori,* Masao Aoki and Kazuhiko Sato



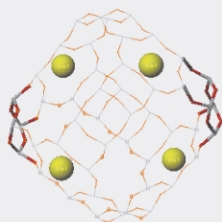
Aqueous H_2O_2 is an ideal oxidant, when coupled with a tungstate complex and a quaternary ammonium hydrogensulfate as an acidic phase-transfer catalyst. It oxidizes alcohols, olefins, and sulfides under organic solvent- and halide-free conditions in an economically, technically, and environmentally satisfying manner.

FEATURE ARTICLE

1987

Controlling chemistry with cations: photochemistry within zeolites

V. Ramamurthy,* J. Shailaja, Lakshmi S. Kaanumalle, R. B. Sunoj and J. Chandrasekhar



Similarly to enzymes, zeolites have well defined reaction cavities and active sites (cations) which could help steer reactions towards a single pathway.

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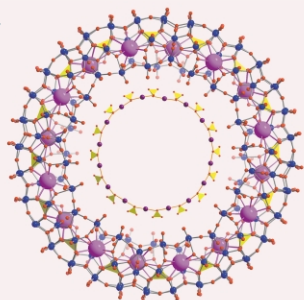
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2000

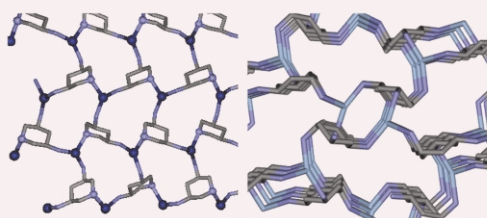


Synergetic activation of “silent receptor” sites leading to a new type of inclusion complex: integration of a 64-membered ring comprising K^+ and SO_4^{2-} ions into a molybdenum oxide-based nanoobject

Achim Müller,* Liviu Toma, Hartmut Bögge, Marc Schmidtman and Paul Kögerler

A molybdenum-oxide-based wheel-shaped parent cluster shows remarkable reactivities, *e.g.* the inclusion of a large number of cations and anions simultaneously.

2002



Controlling dimensionality of silver(I) coordination networks with rigid aliphatic amino ligands: from a 2D to a 3D network of unprecedented topology comprising helical channels

Georg Seeber, Alexandra L. Pickering, De-Liang Long and Leroy Cronin*

Ligand-directed 2D and 3D Ag(I) coordination networks are self-assembled from the rigid, topologically related triamino ligands *cis*-3,5-diaminopiperidine (*cis*-dapi) and *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach) yielding two networks of differing dimensionality including a 3D network of unprecedented topology comprising helical channels.

2004

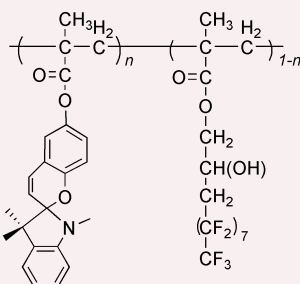


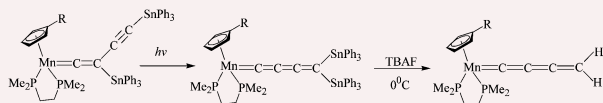
Photo-reversible Pb^{2+} -complexation of insoluble poly(spiropyran methacrylate-*co*-perfluorohydroxy methacrylate) in polar solvents

Takayuki Suzuki,* Yohei Kawata, Shinsuke Kahata and Tatsuya Kato

The first demonstration of photo-reversible Pb^{2+} -complexation of an insoluble spiroropyran-carrying copolymer in aqueous solutions is presented.



2006

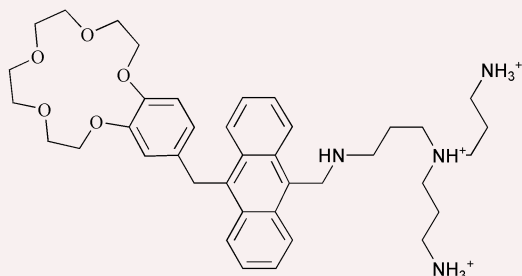


A facile and novel route to unprecedented manganese C_4 cumulenenic complexes

Koushik Venkatesan, Francisco J. Fernández, Olivier Blacque, Thomas Fox, Montserrat Alfonso, Helmut W. Schmalle and Heinz Berke*

The theoretically characterized (DFT) C_4 cumulenenic species $Mn(C_5H_4R)(dmpe) \{-C=C=C=C(SnPh_3)_2\}$ was obtained by photolysis of the C_{sp^2} -Sn bond in $Mn(C_5H_4R)(dmpe) [C=C(SnPh_3)-C\equiv CSnPh_3]$. The tin groups can be removed to generate $Mn(C_5H_4R)(dmpe) \{-C=C=C=C(H)_2\}$.

2010



Direct detection of ion pairs by fluorescence enhancement

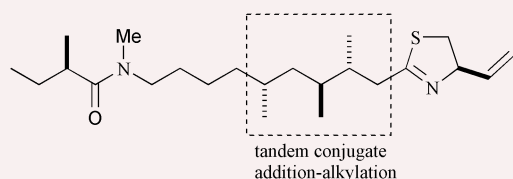
A. Prasanna de Silva, Gareth D. McClean and Sara Pagliari

Sensor 1 signals the simultaneous presence of sodium and phosphate with an increased fluorescence signal in the manner of a photoionic AND logic gate.

2012

Total synthesis of (+)-kalkitoxin

James D. White,* Chang-Sun Lee and Qing Xu

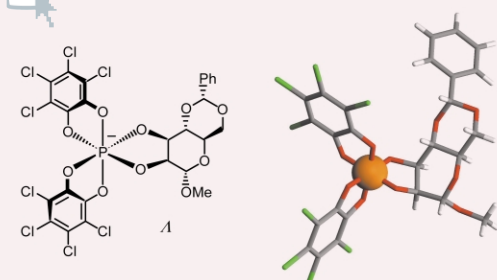


A sixteen-step sequence to kalkitoxin is described which proceeds in *ca.* 3% overall yield.

2014

Mannose derived hexacoordinated phosphate—a generally efficient chiral anion for asymmetric applications

Céline Pérollier, Samuel Constant, Jonathan J. Jodry, Gérald Bernardinelli and Jérôme Lacour*

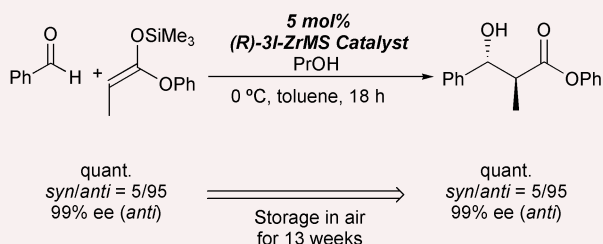


Mannose derived hexacoordinated phosphate—prepared in two steps from methyl- α -D-mannopyranoside—is a chiral anionic auxiliary with broad asymmetric efficiency.

2016

An air-stable, storable chiral zirconium catalyst for asymmetric aldol reactions

Shū Kobayashi,* Susumu Saito, Masaharu Ueno and Yasuhiro Yamashita

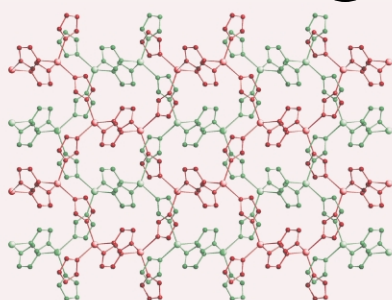


We have developed an air-stable, storable chiral Lewis acid catalyst (3I-ZrMS) for highly stereoselective aldol reactions. This catalyst can be stored for more than three months in air at room temperature without loss of activity.

2018

Synthesis and *ab-initio* XRPD structure of group 12 imidazolato polymers

Norberto Masciocchi,* G. Attilio Ardizzoia,* Stefano Brenna, Fulvio Castelli, Simona Galli, Angelo Maspero and Angelo Sironi

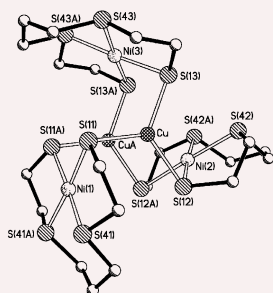


Ab-initio XRPD methods have been used to disclose the peculiar structural features of two new 3D imidazolates, Cd(im)₂ and Hg(im)₂, as well as those of [Hg(im)]NO₃, which contains 1D polycations of [Hg(im)]_n⁺⁺ formulation.

2020

Pinwheel motifs: formation of unusual homo- and hetero-nuclear aggregates *via* bridging thiolates

Angelo J. Amoroso, Simon S. M. Chung, Douglas J. E. Spencer, Jonathan P. Danks, Mark W. Glenny, Alexander J. Blake, Paul A. Cooke, Claire Wilson and Martin Schröder*

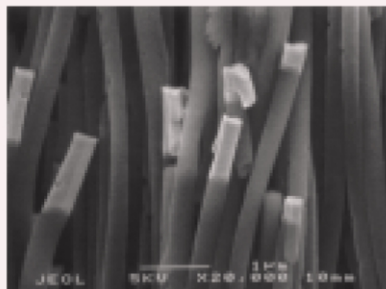


The formation of the hexanuclear and pentanuclear pinwheel aggregates, [Ni₂{Ni(L¹)₄}(BF₄)₄], [Pd₂{Pd(L²)₄}(BF₄)₄] and [Cu₂{Ni(L³)₃}(PF₆)₂], based upon bridging polychelate metal-thiolate ligands is described.

2022

Conducting polymeric nanotubes as high performance methanol oxidation catalyst support

Bashyam Rajesh, K. Ravindranathan Thampi,* Jean-Marc Bonard, Hans Jorg Mathieu, Nicolas Xanthopoulos and Balasubramaniam Viswanathan*



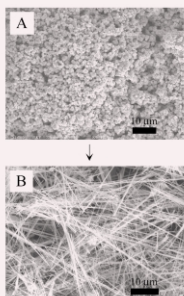
Pt nanoparticles supported on conducting nanotubes of polypyrrole, prepared by a template method, is found to be an excellent catalyst for the electrooxidation of methanol.

2024

Rapid, high yield, solution-mediated transformation of polycrystalline selenium powder into single-crystal nanowires

Bin Cheng and Edward T. Samulski*

A novel, solution phase method opens up a convenient and effective route to large-scale synthesis of single-crystalline trigonal selenium nanowires. The discovery may offer the opportunity to explore numerous applications for these 1-D nanostructures.

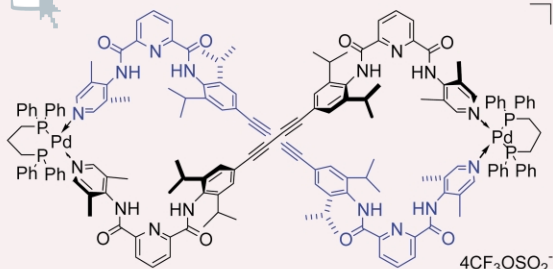


2026

Self-assembly and binding properties of a metallomacrocyclic having two interactive binding subcavities

Sung-Youn Chang, Myoung-Chul Um, Hyounsoo Uh, Hye-Young Jang and Kyu-Sung Jeong*

A coordinate bond-mediated metallomacrocyclic with two topologically discrete subcavities is self-assembled and shows positive allosteric binding behaviours.

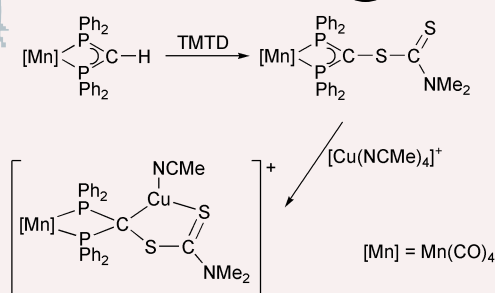


2028

Dithiocarbamyl-substituted diphosphanymethanide complexes of manganese(I): a new type of ambivalent metalloligands

Javier Ruiz,* Roberto Quesada, Víctor Riera, Santiago García-Granda and M. Rosario Díaz

The diphosphanymethanide complex [Mn(CO)₄{(PPh₂)₂C-H}] promotes S-S bond breaking in tetramethylthiuram disulfide (TMTD) affording [Mn(CO)₄{(PPh₂)₂C-S-C(S)NMe₂}], which behaves as versatile metalloligand for the synthesis of heterometallic complexes.

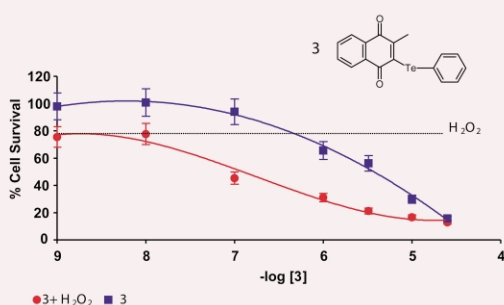


2030

Electrochemical, *in vitro* and cell culture analysis of integrated redox catalysts: implications for cancer therapy

Gregory I. Giles, Niroshini M. Giles, Catriona A. Collins, Kim Holt, Fiona H. Fry, Philip A. S. Lowden, Nicholas J. Gutowski and Claus Jacob*

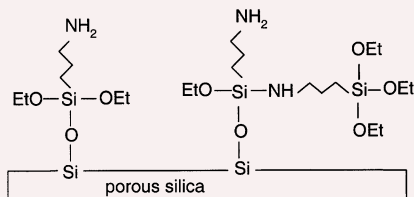
Agents with a combination of quinone and chalcogen redox centres function as catalysts with dual, yet interacting, redox activity that can sensitise cancer cells towards oxidative stress, with implications for anti-cancer therapy.



2032

New bonding modes of gas-phase deposited γ -aminopropyltriethoxysilane on silica studied by ^{29}Si CP/MAS NMR

Satu Ek, Eero I. Iiskola,* Lauri Niinistö, Tuula T. Pakkanen and Andrew Root



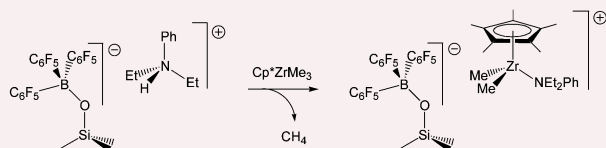
The gas-phase reactions of γ -aminopropyltriethoxysilane (APTS) molecules with the dehydroxylated silica surface were studied by ^{29}Si CP/MAS NMR. The amino ends of APTS molecules were observed to react with the ethoxy groups of other APTS molecules and silanols of silica forming Si–N bonds at the deposition temperatures of 150–300 °C (20–50 mbar).

2034

Supported cationic complexes: selective preparation and characterization of the well-defined electrophilic metallocenium cation

$[\equiv\text{SiO}-\text{B}(\text{C}_6\text{F}_5)_3]^- [\text{Cp}^*\text{ZrMe}_2(\text{Et}_2\text{NPh})]^+$ supported on silica

Nicolas Millot, Catherine C. Santini,* Anne Baudouin and Jean-Marie Basset*

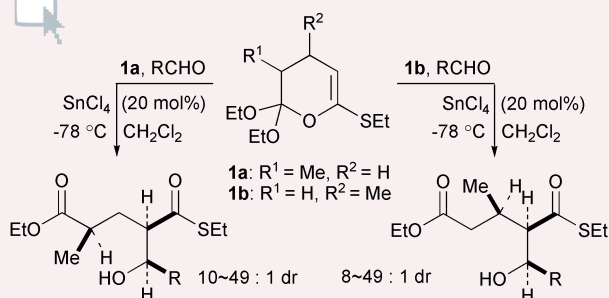


The reaction of Cp^*ZrMe_3 with the heterogeneous activator $[\equiv\text{SiO}-\text{B}(\text{C}_6\text{F}_5)_3]^- [\text{HNEt}_2\text{Ph}]^+$ generate, by an irreversible process of methane elimination, the first well-defined cationic silica-supported metallocenium species $[\equiv\text{SiO}-\text{B}(\text{C}_6\text{F}_5)_3]^- [\text{Cp}^*\text{ZrMe}_2(\text{NEt}_2\text{Ph})]^+$ as an active olefin polymerisation catalyst.

2036

Internal chirality transfer in the reaction of substituted cyclic (*S,O*)-ketene ortho esters with aldehydes catalysed by Lewis acid

Chan-Mo Yu,* Junhee Lee, Ji-Min Kim and Su-Kyung Lee

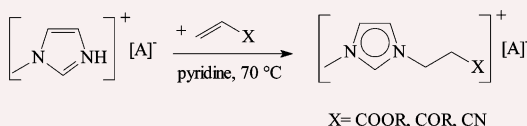


Internal chirality transfer of **1a** and **1b** with aldehydes in the presence of Lewis acid catalyst resulted in high diastereoselectivities in the construction of a highly functionalised acyclic system.

2038

New, functionalised ionic liquids from Michael-type reactions—a chance for combinatorial ionic liquid development

Peter Wasserscheid,* Birgit Drießen-Hölscher, Roy van Hal, H. Christian Steffens and Jörg Zimmermann

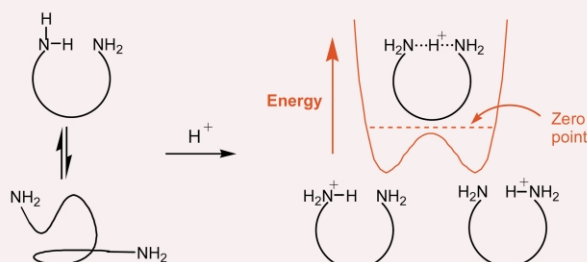


We describe for the first time an alternative and far more efficient method of synthesizing functionalised ionic liquids in a simple, straightforward, two-step synthesis.

2040

cis-1,5-Diaminocyclooctane: the most basic gaseous primary amine?

John C. Poutsma,* Erica J. Andriole, Tristan Sissung and Thomas Hellman Morton*

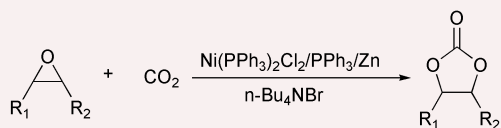


The gas phase basicity of the title compound has been determined to be greater than that of 1,4-diaminobutane, making it the most basic primary diamine measured to date.

2042

A novel and effective Ni complex catalyst system for the coupling reactions of carbon dioxide and epoxides

Fuwei Li, Chungu Xia,* Liwen Xu, Wei Sun and Gexin Chen

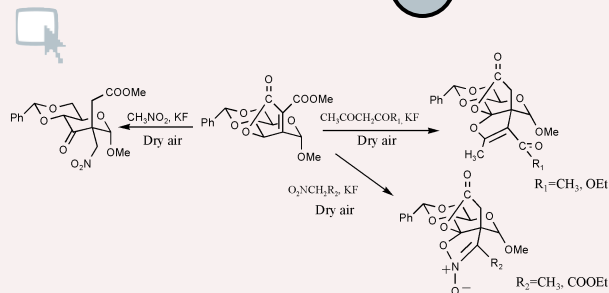
(R₁=CH₃, CH₂Cl, C₂H₅, C₂H₃, C₄H₉, C₆H₅, R₂=H; R₁=R₂=(CH₂)₄)

Coupling of CO₂ and mono-substituted terminal epoxides or cyclohexene oxide to form cyclic carbonates under a Ni complex catalyst system without using co-solvents was achieved in excellent selectivity and TOF.

2044

Stereoselective synthesis of 2,2-bis(*C*-branched-chain)glucopyranosid-3-ulose via an autoxidation–Michael addition reaction

Hong-Min Liu,* Fuyi Zhang and Da-Peng Zou

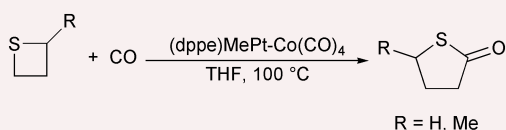


Stereoselective synthesis of 2,2-bis(*C*-branched-chain)-glucopyranosid-3-uloses was achieved from butenolide-containing sugar *via* a novel reaction, the mechanism of which was clarified as autoxidation followed by Michael addition of carbanion.

2046

Catalytic synthesis of thiobutyrolactones via CO insertion into the C–S bond of thietanes in the presence of a heterodinuclear organoplatinum–cobalt complex

Masaki Furuya, Susumu Tsutsuminai, Hiroto Nagasawa, Nobuyuki Komine, Masafumi Hirano and Sanshiro Komiya*



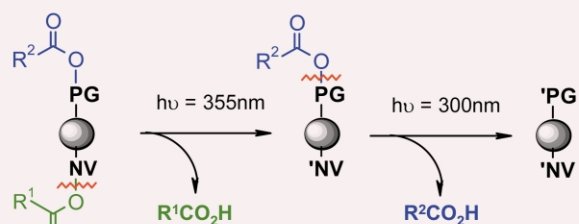
R = H, Me

Heterodinuclear organoplatinum–cobalt complex having a 1,2-bis(diphenylphosphino)ethane ligand (dppe)MePt–Co(CO)₄ catalyzes CO insertion into the C–S bond of thietanes in THF at 100 °C under 1.0 MPa of CO for 2 h to give γ -thiobutyrolactone in quantitative yield.

2048

Wavelength dependent photo-controlled differential release of compounds from solid phase resin

Mark Ladlow,* Coulton H. Legge, Thomas Neudeck, Adrian J. Pipe, Tom Sheppard and Liqun L. Yang



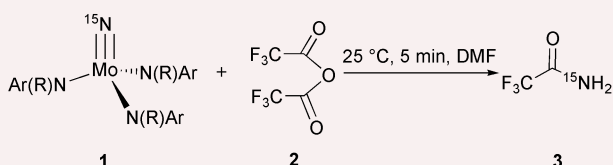
PG = pivaloyl glycol; NV = nitroveratryl

A method to effect the 2-stage controlled photo-mediated differential release of solid phase compound libraries using chromatically orthogonal photolabile linkers attached to the same bifurcated resin beads is described.

2050

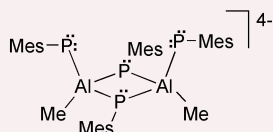
Direct formation of an organonitrogen compound from a molybdenum nitrido species

Huub Henderickx, Gerard Kwakkenbos, Alexander Peters,* Jan van der Spoel and Koen de Vries



A nitrido transition metal species **1** has been coupled to a carbon source **2**, without making use of additional reagents or the necessity of splitting the so formed C–N-coupling product **3** from its former carrier.

2052

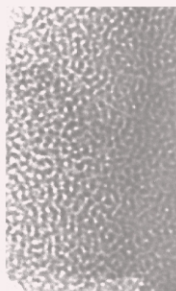


Synthesis and structure of $[\{\text{MeAl}(\mu\text{-PMes})(\text{PMes})\}_2\text{Li}_4\text{]}_2\cdot 7\text{thf}$, containing a $[\text{MeAl}(\mu\text{-PMes})(\text{PMes})]_2^{4-}$ tetraanion (Mes = 2,4,6-Me₃C₆H₂)

Felipe García, Robert Haigh, Mary McPartlin and Dominic S. Wright*

The $[\{\text{MeAl}(\mu\text{-PMes})(\text{PMes})\}_2]^{4-}$ tetraanion is obtained from the reaction of MeAlCl_2 and $\text{MesP}(\text{H})\text{Li}$ in thf, the anion being valence-isoelectronic with the Group 15 anions $[\text{E}(\mu\text{-NR})(\text{NR})]_2^{2-}$.

2054

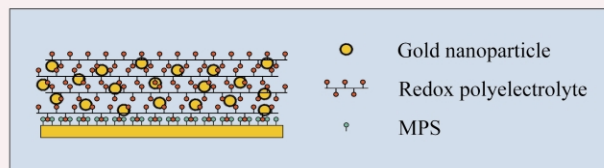


Effect of humidity treatments on porosity and mechanical integrity of mesoporous silica films

Xiaohong Li, Jerome C. Birnbaum,* Rick E. Williford, Glen E. Fryxell, Chris A. Coyle, Glen C. Dunham and Suresh Baskaran

Dramatic increases in elastic moduli are observed for films exposed to humidity at varying temperatures and concentrations, without any significant adverse effects to porosity or dielectric constant. Important results are presented that are of interest in the field of low k materials.

2056

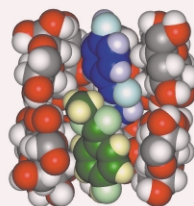
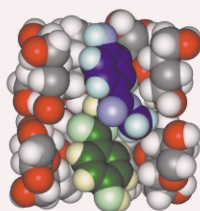


Layer-by-layer self-assembled multilayers of redox polyelectrolytes and gold nanoparticles

Nancy Ferreyra, Liliane Coche-Guérente, Julien Fatisson, Manuel Lopez Teijelo and Pierre Labbé*

Construction and characterization of structural and charge transport properties of electrostatically LbL self-assembled multilayers of gold nanoparticles and a viologen-based redox-active polyelectrolyte is reported.

2058

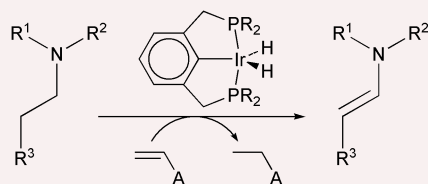


Crystallization of two forms of a cyclodextrin inclusion complex containing a common organic guest

Mino R. Caira,* Elise J. C. de Vries and Luigi R. Nassimbeni

Depending on the crystallization conditions, both triclinic and monoclinic inclusion complexes between β -cyclodextrin and methylparaben (4-hydroxybenzoic acid methyl ester) can be isolated.

2060



Novel synthesis of enamines by iridium-catalyzed dehydrogenation of tertiary amines

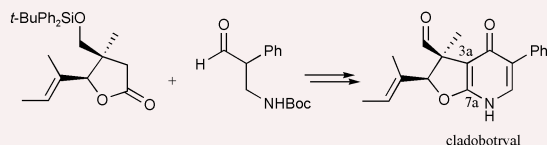
Xiawei Zhang, Amy Fried, Spencer Knapp* and Alan S. Goldman*

A novel route to enamines is reported, the dehydrogenation of tertiary amines catalyzed by a “pincer-ligated” iridium catalyst.

2062

First synthesis of the antifungal and antibacterial agent cladobotryal

Derrick L. J. Clive* and Xiaojun Huang

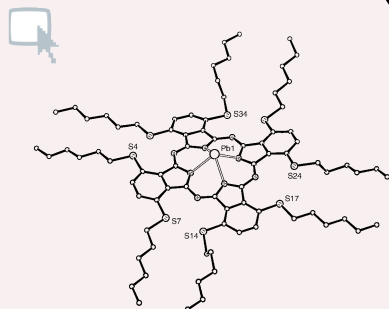


The quaternary center of the lactone component was generated by radical cyclization, and the C(3a)–C(7a) double bond was formed by tautomerization of an imine, a key step that set the stage for imine formation being replacement of *N*-Boc by *N*-CO₂SiPr-*i*₃.

2064

Structural characterisation of a red phthalocyanine

Paul M. Burnham, Michael J. Cook,* Lee A. Gerrard, Martin J. Heeney and David L. Hughes

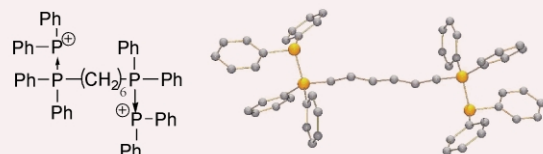


Metal 1,4,8,11,15,18,22,25-octakis(hexylsulfanyl)phthalocyanines exhibit a weak absorption band in the 450–600 nm region, leading to novel dyes that include the red lead metallated derivative that has been characterised by X-ray crystallography.

2066

Homoatomic P → P coordination: A versatile synthetic approach to polyphosphorus dications

Neil Burford,* Paul J. Ragnogna, Robert McDonald and Michael J. Ferguson

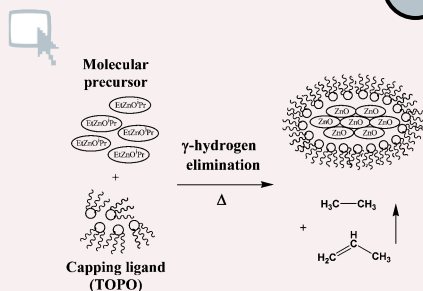


Polyphosphorus dications have been synthesised and comprehensively characterised as diphosphine (dppe, dmpe and dpph) linked Ar₂P⁺ Lewis acids (Ar = C₆H₅); this application of unique homoatomic coordination chemistry provides important building blocks for extended systems.

2068

Monodispersed ZnO nanoparticles from a single molecular precursor

Chang G. Kim, Kiwhan Sung, Taek-Mo Chung, Duk Y. Jung and Yunsoo Kim*

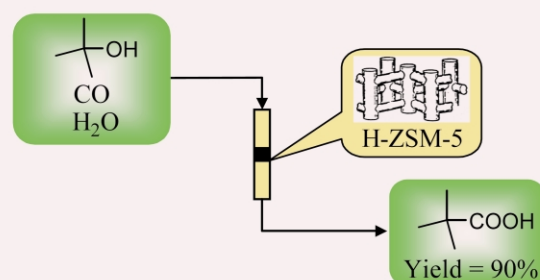


Thermolysis of a mixture of the single molecular precursor EtZnO⁺Pr and a capping ligand without any oxygen source produces monodispersed ZnO nanoparticles through γ -hydrogen elimination reaction.

2070

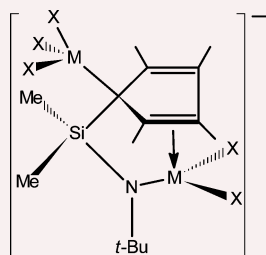
Highly active and stable performance of catalytic vapor phase Koch-type carbonylation of *tert*-butyl alcohol over H-zeolites

Tao Li, Nobuko Tsumori, Yoshie Souma and Qiang Xu*



A high catalytic activity and excellent stability of the vapor phase Koch-type carbonylation of *tert*-butyl alcohol towards 2,2-dimethylpropanoic acid on a H-ZSM-5 catalyst were achieved with a yield as high as 90% without any threat of deactivation in 120 h.

2072



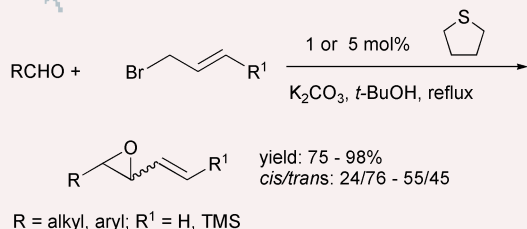
M = Ga, X = Cl; M = In, X = Br

An unprecedented mode of ligation for a bridged amido-cyclopentadienide (constrained geometry) ligand; π -olefinic interactions with gallium and indium

Jeffrey M. Pietryga, Jamie N. Jones, Lucille A. Mullins, Robert J. Wiacek and Alan H. Cowley*

Treatment of the di-Grignard reagent $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}-t\text{-Bu})](\text{MgCl})_2\cdot\text{THF}$ with GaCl_3 or InBr_3 in THF solution results in salts of bimetallic anions of the type $[\text{X}_3\text{M}\{\text{C}_5\text{Me}_4(\text{N}-t\text{-Bu})\}\text{MX}_2]^-$.

2074

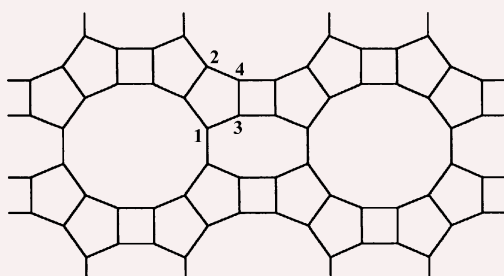
R = alkyl, aryl; R¹ = H, TMS

A facile tetrahydrothiophene-catalyzed ylide route to vinyloxiranes

Kai Li, Xian-Ming Deng and Yong Tang*

Access to vinyloxiranes using aldehydes and allylic bromides in the presence of 1–5 mol% tetrahydrothiophene is reported. Both aliphatic and aromatic aldehydes work well in this reaction and the catalyst loading could be reduced as low as 0.5 mol%.

2076

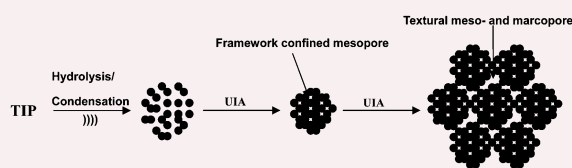


Identification of distinct Brønsted acidic sites in zeolite mordenite by proton localization and ^{27}Al - ^1H REAPDOR NMR

Subramanian Ganapathy,* Rajiv Kumar, Laurent Delevoye and Jean-Paul Amoureux

^{27}Al - ^1H REAPDOR NMR distinguishes structurally non-equivalent tetrahedral aluminium sites in Mordenite

2078



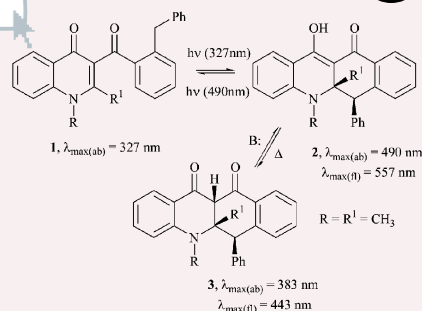
TIP: Titanium isopropoxide ● Titanium Oxide Sol Particle UIA: Ultrasound-Induced Agglomeration (or Aggregation)

A sonochemical approach to hierarchical porous titania spheres with enhanced photocatalytic activity

Lizhi Zhang and Jimmy C. Yu*

Hierarchical porous titania spheres were prepared sonochemically in the presence of a triblock copolymer; the textural meso-/macroporosity of the new material has a positive effect on its photocatalytic activity.

2080

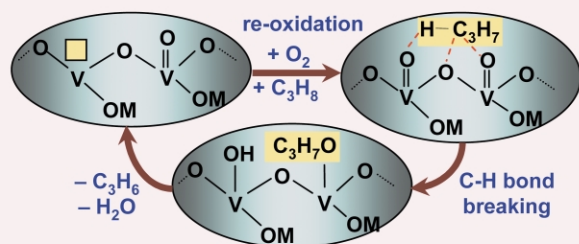


A novel photoreversible photochromic system involving a hydrogen transfer/cyclization sequence

Vladimir Lokshin,* Magali Valès, André Samat, Gérard Pèpe, Anatoly Metelitsa and Vladimir Khodorkovsky*

A novel photoreversible photochromic system, 3-(2-benzylbenzoyl)-1,2-R,R¹-4(1H)-quinolinones/12-hydroxy-5-R-5a-R¹-6-phenyl-5a,6-dihydrobenzo[b]acridin-11(5H)-ones, is described.

2082

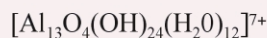
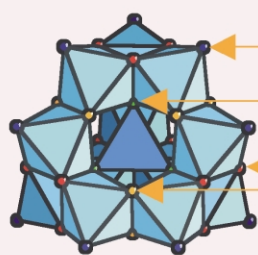


In situ UV-visible assessment of extent of reduction during oxidation reactions on oxide catalysts

Morris D. Argyle, Kaidong Chen, Carlo Resini, Catherine Krebs, Alexis T. Bell* and Enrique Iglesia*

The extent of reduction of active centers was measured from pre-edge UV-visible spectral features during propane oxidative dehydrogenation on $\text{VO}_x/\text{Al}_2\text{O}_3$ and found to increase with increasing VO_x domain size and propane/ O_2 ratio.

2084



• $\eta\text{-OH}_2$

• $\mu_4\text{-O}$

• $\mu_2\text{-OH T}$

• $\mu_2\text{-OH iT}$

Fluorination of the ϵ -Keggin Al_{13} polycation

Lionel Allouche and Francis Taulelle

Fluorination of the ϵ -Keggin Al_{13} polycation, substitutes di- μ_2 -OH bridges, and enhances the formation of Al_{30} . Fluorination might be the method of choice to grow polycations to the size of giant polyanions.

ADDITIONS AND CORRECTIONS

2086

Frederik Claeysens, Neil L. Allan, Paul W. May, Pablo Ordejón and Josep M. Oliva

Solid phosphorus carbide?

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