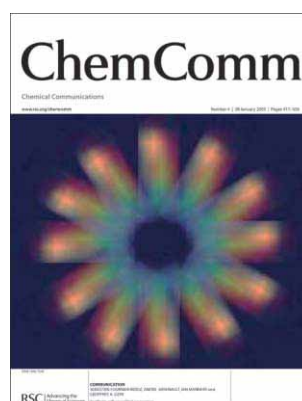




Cover
Synthesis of certain catalysts on a kilogram scale at a Degussa plant in Hanau (Germany). See p. 431.



Inside cover
A silicon tethered nanorod rotor in action. See p. 441.

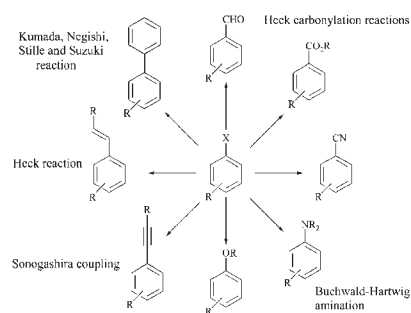
FEATURE ARTICLE

431

The development of efficient catalysts for palladium-catalyzed coupling reactions of aryl halides

Alexander Zapf* and Matthias Beller*

In the mid 1990s a program was started on the development of more efficient palladium catalysis for the C–C and C–N coupling reactions of aryl halides, especially aryl chlorides. In this contribution, investigations on new catalyst systems and their applications in organic synthesis are summarized.



COMMUNICATIONS

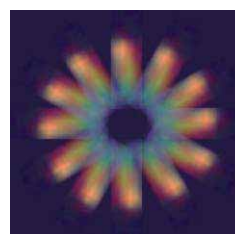
441



Synthetic self-propelled nanorotors

Sébastien Fournier-Bidoz, André C. Arsenault, Ian Manners* and Geoffrey A. Ozin*

Self-powered nanorotors have been prepared from barcoded gold–nickel nanorods having the gold end anchored to the surface of a silicon wafer. Constant velocity circular movements are observed when hydrogen peroxide fuel is catalytically decomposed to oxygen at the unattached nickel end of the nanorod.



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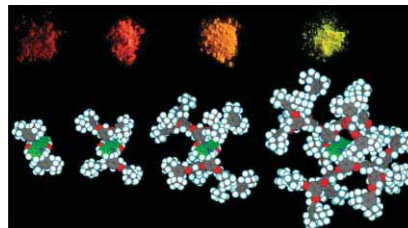
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444

Dendritic incorporation of quinacridone: solubility, aggregation, electrochemistry, and solid-state luminescence

Adrian Ortiz, Ware H. Flora, Gemma D. D'Ambruoso, Neal R. Armstrong* and Dominic V. McGrath*

Dendrimization of quinacridone successfully inhibits aggregation and self-absorption between core molecules in the solid state, with corresponding increases in luminescence efficiency.

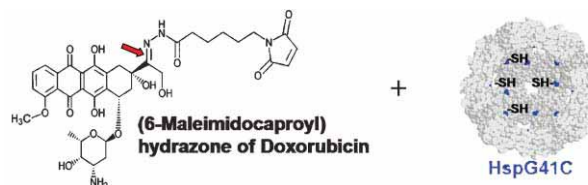


447

Selective attachment and release of a chemotherapeutic agent from the interior of a protein cage architecture

Michelle L. Flenniken, Lars O. Liepold, Bridgid E. Crowley, Deborah A. Willits, Mark J. Young and Trevor Douglas

The antitumor agent doxorubicin was covalently bound and selectively released in a pH dependent manner from the interior surface of a genetically modified small heat shock protein (Hsp) cage.

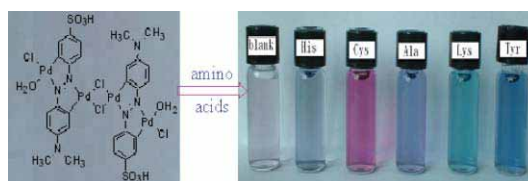


450

A cyclometalated palladium–azo complex as a differential chromogenic probe for amino acids in aqueous solution

Shun-Hua Li, Chun-Wei Yu and Jin-Gou Xu*

A cyclometalated palladium–azo complex as a sensitive chromogenic probe for α -amino acids in aqueous solution is described. Different amino acids were distinguishable in their UV-vis absorption responses.

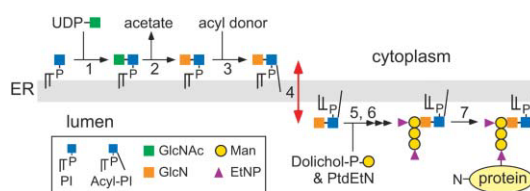


453

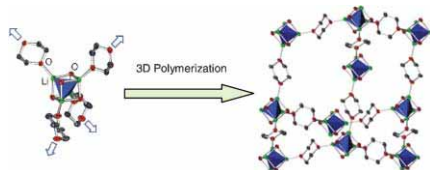
Flip-flop of glycosylphosphatidylinositols (GPI's) across the ER

Ram A. Vishwakarma* and Anant K. Menon*

The ATP-independent, protein-dependent transbilayer flip-flop of early intermediates in the glycosylphosphatidylinositol (GPI) biosynthetic pathway has been demonstrated using novel, acyl-NBD-labeled fluorescent GPI probes and a biochemical reconstitution approach.



456

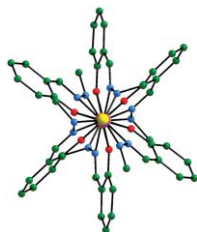


Use of tetrameric cubane aggregates of lithium aryloxides as secondary building units in controlling network assembly

Dugald J. MacDougall, J. Jacob Morris, Bruce C. Noll and Kenneth W. Henderson*

Readily prepared $\text{Li}_4(\text{OAr})_4$ molecular cubanes can be used as building blocks in the rational construction of closely related one-, two- and three-dimensional polymers.

459

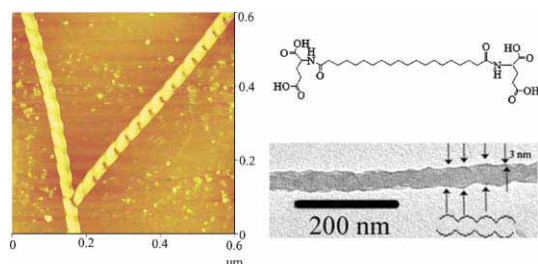


A luminescent linear trinuclear magnesium complex assembled from a phosphorus-based tris-hydrazone ligand

Vadapalli Chandrasekhar,* Ramachandran Azhakar, Jamie F. Bickley and Alexander Steiner

Synthesis of a novel linear trinuclear complex from a phosphorus-based tris-hydrazone ligand and its luminescent properties in solution and solid-state are described.

462

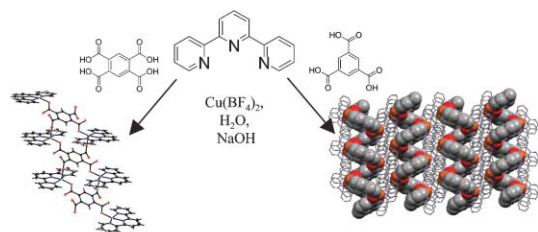


Self-assembled helical spherical-nanotubes from an L-glutamic acid based bolaamphiphilic low molecular mass organogelator

Chuanlang Zhan, Peng Gao and Minghua Liu*

An L-glutamic acid based bolaamphiphilic low molecular mass organogelator with an interesting helical spherical-nanotube structure was synthesized, which can gel a 1 : 1 mixture of ethanol (methanol)-water solvents in a low concentration of less than 0.3%.

465



Helical and polymeric nanostructures assembled from benzene tri- and tetracarboxylic acids associated with terpyridine copper(II) complexes

Pingshan Wang, Charles N. Moorefield, Matthew Panzer and George R. Newkome*

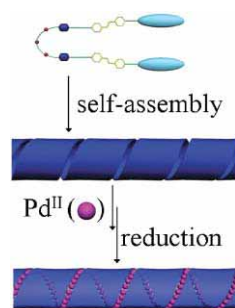
The change of a single carboxyl moiety produces dramatically different crystal architectures.

468

Spatial organization and patterning of palladium nanoparticles on a self-assembled helical ribbon lipid

Jong Hwa Jung,* Jeong Ah Rim, Soo Jin Lee and Shim Sung Lee

A cholesterol derivative **1** forms self-assembled helical ribbons in organic solvent, and treatment of this helical ribbon lipid as a template with Pd(Ac)₂ provides helically-patterned arrays of palladium nanoparticles followed by reduction.

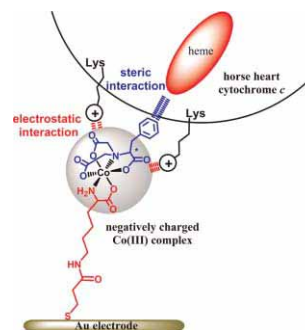


471

Self-assembled monolayers of optically active Co(III) complexes: a new promoter electrode recognizing the electron transfer site in cytochrome *c*

Isao Takahashi, Tomohiko Inomata, Yasuhiro Funahashi, Tomohiro Ozawa, Koichiro Jitsukawa and Hideki Masuda*

A new-class of promoter electrode bearing a molecular recognition ability has been constructed; the chirality and/or orientation of promoter on the Au electrode surface have affected the electron transfer rate of cytochrome *c*.

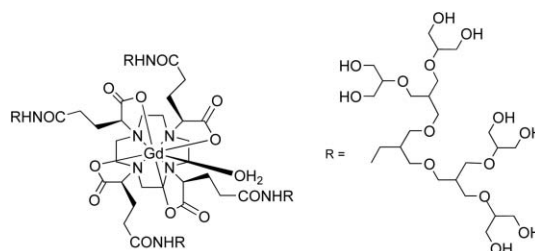


474

Efficient relaxivity enhancement in dendritic gadolinium complexes: effective motional coupling in medium molecular weight conjugates

David A. Fulton, Mark O'Halloran, David Parker,* Kanthi Senanayake, Mauro Botta and Silvio Aime

The Gd ion lies at the barycentre of the dendritic structure and lies on any axis of reorientational motion leading to gains in inner and second sphere relaxivities at MRI imaging fields.

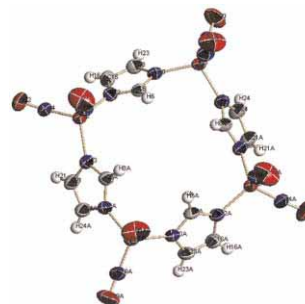


477

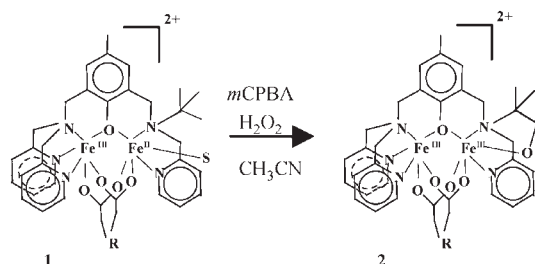
A cyclic tetra-nuclear dinitrosyl iron complex [Fe(NO)₂(imidazole)₄]₄: synthesis, structure and stability

Ximeng Wang, Eric B. Sundberg, Lijuan Li,* Katherine A. Kantardjieff, Steven R. Herron, Mark Lim and Peter C. Ford

A cyclic tetrameric dinitrosyliron complex [Fe(NO)₂(Im-H)₄]₄ was synthesized and showed NO release under thermal conditions. In donor solvents this fragments into monomeric units that give EPR spectra analogous to the *g* = 2.03 species seen in mammalian biology.



480

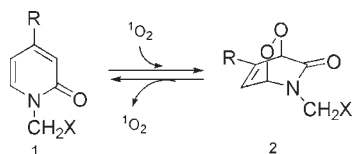


A diiron complex mediates an intramolecular aliphatic hydroxylation by various oxygen donors

Frédéric Avenier, Lionel Dubois, Patrick Dubourdeaux and Jean-Marc Latour*

The dangling *tert*-butyl residue **1** is quantitatively oxygenated to the butanolate **2** by H_2O_2 or *m*-CPBA. ^{18}O labelling experiments reveal that H_2O_2 , but not *m*-CPBA, reacts akin to mononuclear complexes.

483

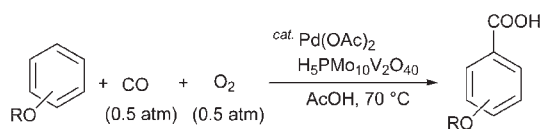


Reversible 1,4-cycloaddition of singlet oxygen to *N*-substituted 2-pyridones: 1,4-endoperoxide as a versatile chemical source of singlet oxygen

Masakatsu Matsumoto,* Masayo Yamada and Nobuko Watanabe

$^1\text{O}_2$ adds to nitrogen-analogues of α -pyranone, namely, *N*-substituted pyridones (**1**) to afford 1,4-endoperoxides (**2**) exclusively, and the thus-obtained peroxides (**2**) liberate $^1\text{O}_2$ in high yield.

486

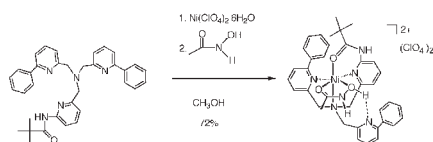


Carboxylation of anisole derivatives with CO and O_2 catalyzed by $\text{Pd}(\text{OAc})_2$ and molybdovanadophosphates

Shinichiro Ohashi, Satoshi Sakaguchi and Yasutaka Ishii*

Anisole and its homologues were carboxylated under the influence of CO and O_2 catalyzed by $\text{Pd}(\text{OAc})_2$ combined with molybdovanadophosphates (HPMoV) under mild conditions to give the corresponding carboxylic acids in fair to good yields.

489



Neutral acetohydroxamic acid coordination to a mononuclear Ni(II) center stabilized by an intramolecular hydrogen-bonding interaction

Katarzyna Rudzka, Magdalena M. Makowska-Grzyska, Ewa Szajna, Atta M. Arif and Lisa M. Berreau*

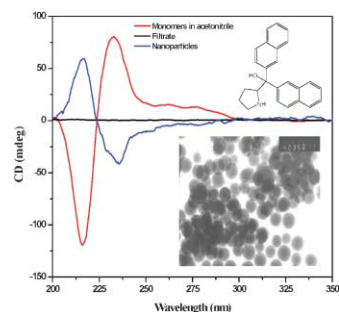
A novel mononuclear Ni(II) complex having a coordinated neutral acetohydroxamic acid ligand was isolated using a chelate ligand that provides an internal hydrogen bond acceptor.

492

CD inversion and fluorescence enhancement in organic nanoparticles of (*R*)-di-2-naphthylprolinol

Lu Xi, Hongbing Fu, Wensheng Yang and Jiannian Yao*

The positive exciton coupling circular dichroism (ECCD) exhibited by monomer of (*R*)-di-2-naphthylprolinol in organic solvent is inverted to be negative upon the formation of its nanoparticles.

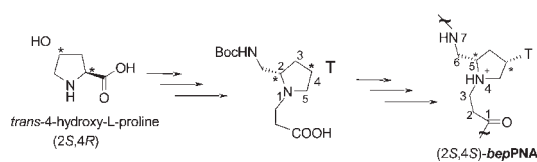


495

Backbone-extended pyrrolidine peptide nucleic acids (*bep*PNA): design, synthesis and DNA/RNA binding studies

T. Govindaraju and Vijjayanti A. Kumar*

One-carbon extended conformationally constrained pyrrolidine PNA monomer has been synthesized from naturally occurring *trans*-4-hydroxy-L-proline and incorporated into PNA sequences at predefined positions. Backbone-extended pyrrolidine peptide nucleic acids (*bep*PNA) showed differential DNA/RNA binding affinity depending on the position and number of modifications.

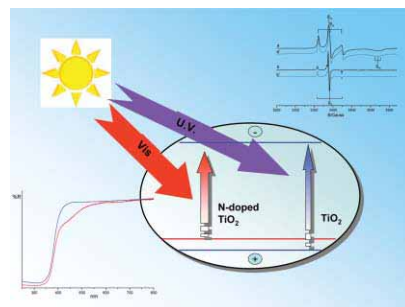


498

The nature of paramagnetic species in nitrogen doped TiO₂ active in visible light photocatalysis

Stefano Livraghi, Annamaria Votta, Maria Cristina Paganini and Elio Giamello*

Nitrogen doped TiO₂, a novel photocatalyst active in the decomposition of organic pollutants using visible light, contains two different types of paramagnetic centres (neutral NO radicals and NO₂²⁻ type radical ions respectively) which are likely related to specific properties of the solid.

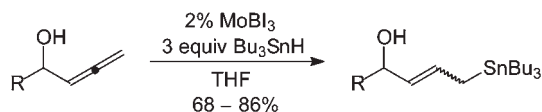


501

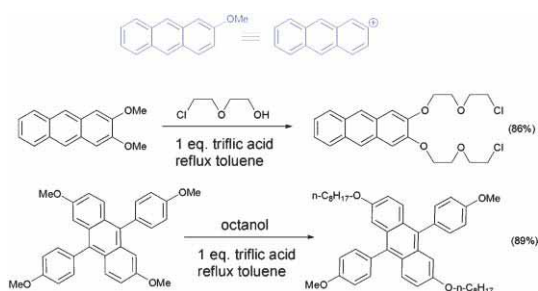
Molybdenum-catalyzed hydrostannations of allenylcarbinols

Uli Kazmaier* and Manuela Klein

Allenylcarbinols undergo regioselective hydrostannation in the presence of MoBI₃, a catalyst originally developed for the hydrostannation of alkynes, giving rise to allylstannanes.



504

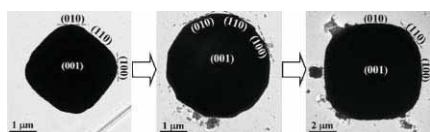


Synthesis of anthracene ethers from anthracene methyl ethers *via* an acid-catalyzed exchange reaction

Chih-Hsiu Lin* and Krishnan Radhakrishnan

We have developed a general synthesis of anthracene ethers *via* acid-catalyzed exchange reactions. The net reaction conveys anthracene methyl ether as an anthracene cation synthon, granting convenient entry into various anthracene derivatives for potential supramolecular assemblies and electronic devices.

507

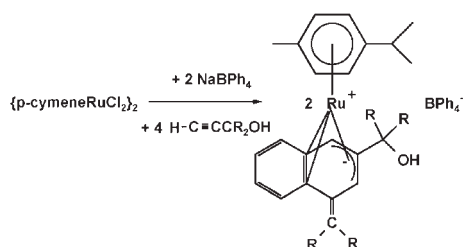


Solution route to single crystalline SnO platelets with tunable shapes

Shuai Wang, Songhai Xie, Hexing Li, Shirun Yan, Kangnian Fan and Minghua Qiao*

Square and round single crystalline SnO platelets were prepared in a solution-based chemical route aided with sonication at room temperature.

510



Coupling of alkynols and a phenyl group to a novel η^5 -dihydronaphthalenide ligand on a ruthenium template

Jadranka Čubrilo, Rainer F. Winter* and Dietrich Gudat

$\{p\text{-cymene}\}\text{RuCl}_2\}_2$ promotes the stoichiometric coupling of a phenyl group and two equivalents of a disubstituted alkyne to unprecedented η^5 -1-methylene-1,2-dihydronaphthalenide ligands in a reaction involving BPh_4^- as a phenylating agent.

513



Fluorescence enhancement of a signaling system in the simultaneous presence of transition and alkali metal ions: a potential *AND* logic gate

Bamaprasad Bag and Parimal K. Bharadwaj*

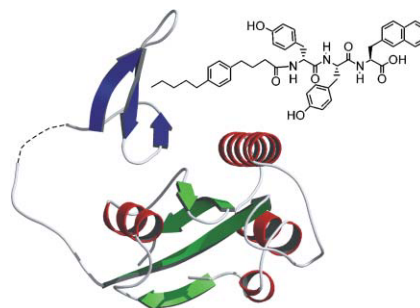
Fluorescence enhancement of a signaling system L_1 in simultaneous presence of a transition metal ion and an alkali metal ion that mimics the function of an *AND* logic gate.

516

Identification of *hPin1* inhibitors that induce apoptosis in a mammalian Ras transformed cell line

Elena Bayer, Michael Thutewohl, Claudia Christner, Thomas Tradler, Frank Osterkamp, Herbert Waldmann and Peter Bayer*

Human Pin1, a phosphate specific prolyl isomerase, has become an interesting target for pharmaceutical cancer therapy. Inhibition of the enzyme in transformed cell lines induces apoptosis, whereas normal tissues are hardly influenced. The authors have developed a class of potent Pin1 inhibitors and investigated their mechanism of action.

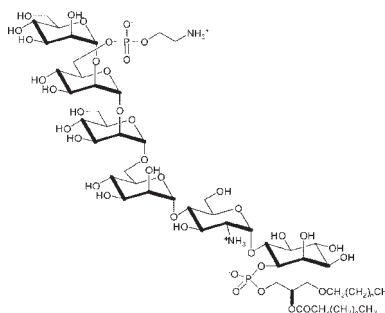


519

A new approach to construct full-length glycosylphosphatidylinositols of parasitic protozoa and [4-deoxy-Man-III]-GPI analogues

Asif Ali, D. Channe Gowda and Ram A. Vishwakarma*

A new [2 + 2 + 2] approach to construct GPI molecules through the efficient synthesis of glucosamine-inositol and tetramannose intermediates led to a total synthesis of a GPI-anchor of *Trypanosoma cruzi*, and also afforded a key intermediate for the synthesis of valuable [4-deoxy-Man-III]-GPI analogues.

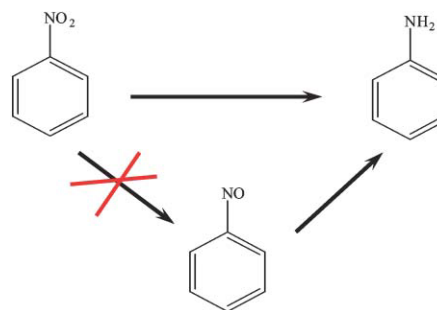


522

The hydrogenation of nitrobenzene to aniline: a new mechanism

Elaine A. Gelder, S. David Jackson* and C. Martin Lok

The Haber mechanism for nitrobenzene hydrogenation has been superseded; a new mechanism where nitrosobenzene is not an intermediate has been proposed.

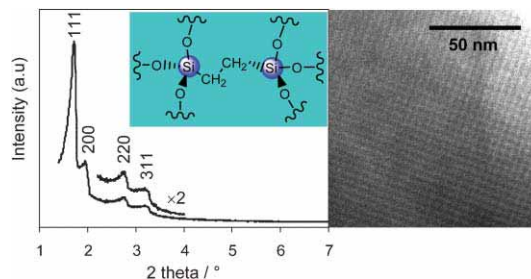


525

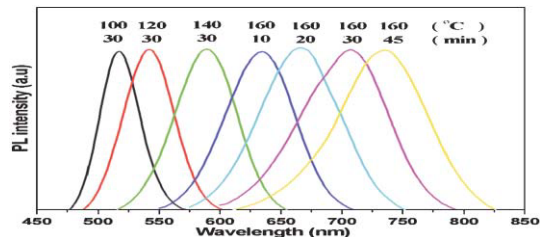
PMO[KIT-5]-n: synthesis of highly ordered three-dimensional periodic mesoporous organosilicas with *Fm3m* symmetry

Yucang Liang, Marianne Hanzlik and Reiner Anwänder*

1,2-Bis(triethoxysilyl)ethane (BTEE) can be converted into completely cross-linked, topologically new organosilicas by using divalent surfactant $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_2(\text{CH}_2)_3\text{N}(\text{CH}_3)_3]^{2+}2\text{Br}^-$ (C_{16-3-1}) as a structure directing agent (SDA) under basic hydrothermal reaction conditions.



528

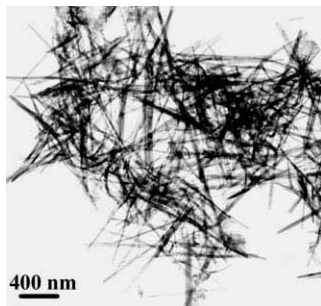


Rapid synthesis of highly luminescent CdTe nanocrystals in the aqueous phase by microwave irradiation with controllable temperature

Liang Li, Huifeng Qian and Jicun Ren*

A rapid aqueous synthesis of broad size range CdTe nanocrystals with high quantum yield by microwave irradiation with controllable temperature.

531

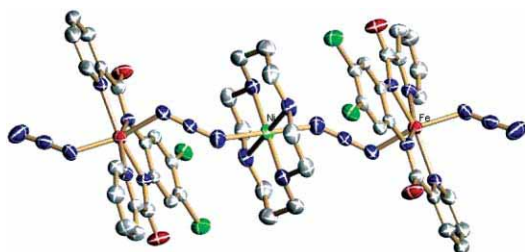


Protein-assisted synthesis of single-crystal nanowires of bismuth compounds

Feng Gao, Qingyi Lu and Sridhar Komarneni*

Protein lysozyme has been found to be a new morphology-directing reagent and by this simple and mild bio-molecule assisted method single-crystal bismuth compound nanowires could be synthesized.

534

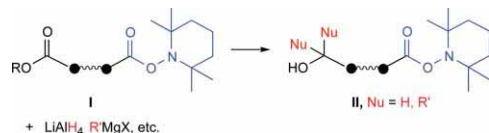


Rational design of azide-bridged bimetallic complexes. Crystal structure and magnetic properties of $\text{Fe}^{\text{III}}\text{MFe}^{\text{III}}$ ($\text{M} = \text{Ni}^{\text{II}}$ and Cu^{II}) trinuclear species

Enrique Colacio,* Jean-Pierre Costes, José M. Domínguez-Vera, Ikram Ben Maimoun and José Suárez-Varela

The first examples of azide-bridged bimetallic trinuclear complexes $\{[\text{M}(\text{cyclam})][\text{FeL}(\text{N}_3)(\mu_{1,5}\text{-N}_3)_2]\}$ ($\text{M} = \text{Ni}(\text{II})$, $\text{Cu}(\text{II})$; $\text{H}_2\text{L} = 4,5\text{-dichloro-1,2-bis}(\text{pyridine-2-carboxamido})\text{benzene}$) have been prepared and structurally characterized. The magnetic study revealed the existence of irregular spin state structures with antiferro- and ferromagnetic interactions, respectively.

537



Reactivity of *N*-alkanoyloxy-2,2,6,6-tetramethylpiperidines (*O*-acylTEMPOs) towards hydride-transferring or metallic alkylating reagents; unprecedented stability and application to chemoselective transformations

Tsutomu Inokuchi,* Hiroyuki Kawafuchi and Junzo Nokami

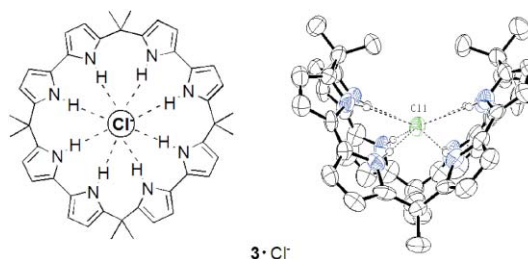
Chemoselective transformations of diacid mixed alkyl/TEMP-1-yl esters, where *O*-acylTEMPOs remained intact, were achieved with hydride-transferring and metallic alkylating reagents, *i.e.*, LiAlH_4 , $\text{R}'\text{MgX}$, *etc.*, giving the corresponding carbinols.

540

Calix[4]bipyrrole—a big, flexible, yet effective chloride-selective anion receptor

Jonathan L. Sessler,* Deqiang An, Won-Seob Cho, Vincent Lynch and Manuel Marquez

Calix[4]bipyrrole, in spite of being large and flexible, is able to adopt conformations that allow it to stabilize the formation of “nested” chloride and bromide complexes in the solid state and to bind chloride anion well in acetonitrile solution.

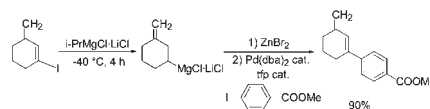


543

Preparation of cyclic alkenylmagnesium reagents *via* an iodine/magnesium exchange

Hongjun Ren, Arkady Krasovskiy and Paul Knochel*

Various cyclic alkenyl and dienyl Grignard reagents can be readily prepared *via* an I/Mg-exchange using the new reagent *i*-PrMgCl·LiCl.

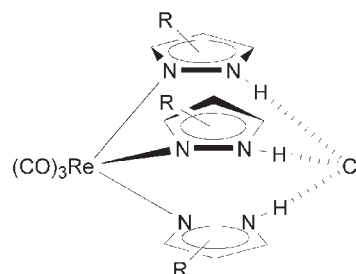


546

Cationic *fac*-tris(pyrazole) complexes as anion receptors

Sonia Nieto, Julio Pérez,* Víctor Riera, Daniel Miguel and Celedonio Alvarez

The “anti-scorpionate” compounds *fac*-[Re(CO)₃(pz)₃]BAR'₄, easily prepared *via* reactions of [Re(OTf)(CO)₃] with three equivalent of the appropriate pyrazole (pz) and NaBAR'₄, are stable against pyrazole dissociation and display a high affinity toward chloride, being the first examples of the tris(pyrazole) receptors proposed one decade ago.

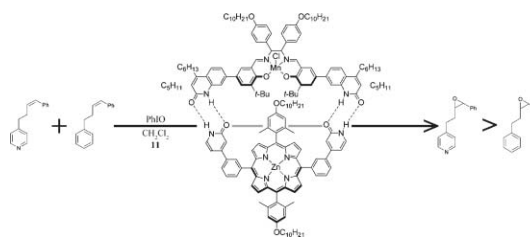


549

A dynamic supramolecular system exhibiting substrate selectivity in the catalytic epoxidation of olefins

Stefán Jónsson, Fabrice G. J. Odille, Per-Ola Norrby and Kenneth Wärnmark*

A dynamic supramolecular system involving hydrogen bonding between a Mn(III) salen catalyst and a Zn(II) porphyrin receptor exhibits selectivity for pyridine appended *cis*- β -substituted styrene derivatives over phenyl appended derivatives in a catalytic epoxidation reaction.




AUTHOR INDEX

- Aime, Silvio, 474
 Ali, Asif, 519
 Alvarez, Celedonio, 546
 An, Deqiang, 540
 Anwander, Reiner, 525
 Arif, Atta M., 489
 Armstrong, Neal R., 444
 Arsenaault, André C., 441
 Avenier, Frédéric, 480
 Azhakar, Ramachandran, 459
 Bag, Bamaprasad, 513
 Bayer, Elena, 516
 Bayer, Peter, 516
 Beller, Matthias, 431
 Berreau, Lisa M., 489
 Bharadwaj, Parimal K., 513
 Bickley, Jamie F., 459
 Botta, Mauro, 474
 Chandrasekhar, Vadapalli, 459
 Cho, Won-Seob, 540
 Christner, Claudia, 516
 Colacio, Enrique, 534
 Costes, Jean-Pierre, 534
 Crowley, Bridgid E., 447
 Čubrilo, Jadranka, 510
 D'Ambruoso, Gemma D., 444
 Domínguez-Vera, José M., 534
 Douglas, Trevor, 447
 Dubois, Lionel, 480
 Dubourdeaux, Patrick, 480
 Fan, Kangnian, 507
 Flenniken, Michelle L., 447
 Flora, Ware H., 444
 Ford, Peter C., 477
 Fournier-Bidoz, Sébastien, 441
 Fu, Hongbing, 492
 Fulton, David A., 474
 Funahashi, Yasuhiro, 471
 Gao, Feng, 531
 Gao, Peng, 462
 Gelder, Elaine A., 522
 Giamello, Elio, 498
 Govindaraju, T., 495
 Gowda, D. Channe, 519
 Gudat, Dietrich, 510
 Hanzlik, Marianne, 525
 Henderson, Kenneth W., 456
 Herron, Steven R., 477
 Inokuchi, Tsutomu, 537
 Inomata, Tomohiko, 471
 Ishii, Yasutaka, 486
 Jackson, S. David, 522
 Jitsukawa, Koichiro, 471
 Jónsson, Stefán, 549
 Jung, Jong Hwa, 468
 Kantardjieff, Katherine A., 477
 Kawafuchi, Hiroyuki, 537
 Kazmaier, Uli, 501
 Klein, Manuela, 501
 Knochel, Paul, 543
 Komarneni, Sridhar, 531
 Krasovskiy, Arkady, 543
 Kumar, Vaijayanti A., 495
 Latour, Jean-Marc, 480
 Lee, Shim Sung, 468
 Lee, Soo Jin, 468
 Li, Hexing, 507
 Li, Liang, 528
 Li, Lijuan, 477
 Li, Shun-Hua, 450
 Liang, Yucang, 525
 Liepold, Lars O., 447
 Lim, Mark, 477
 Lin, Chih-Hsiu, 504
 Liu, Minghua, 462
 Livraghi, Stefano, 498
 Lok, C. Martin, 522
 Lu, Qingyi, 531
 Lynch, Vincent, 540
 MacDougall, Dugald J., 456
 Maimoun, Ikram Ben, 534
 Makowska-Grzyska, Magdalena M., 489
 Manners, Ian, 441
 Marquez, Manuel, 540
 Masuda, Hideki, 471
 Matsumoto, Masakatsu, 483
 McGrath, Dominic V., 444
 Menon, Anant K., 453
 Miguel, Daniel, 546
 Moorefield, Charles N., 465
 Morris, J. Jacob, 456
 Newkome, George R., 465
 Nieto, Sonia, 546
 Nokami, Junzo, 537
 Noll, Bruce C., 456
 Norrby, Per-Ola, 549
 Odille, Fabrice G. J., 549
 O'Halloran, Mark, 474
 Ohashi, Shinichiro, 486
 Ortiz, Adrian, 444
 Osterkamp, Frank, 516
 Ozawa, Tomohiro, 471
 Ozin, Geoffrey A., 441
 Paganini, Maria Cristina, 498
 Panzer, Matthew, 465
 Parker, David, 474
 Pérez, Julio, 546
 Qian, Hui Feng, 528
 Qiao, Minghua, 507
 Radhakrishnan, Krishnan, 504
 Ren, Hongjun, 543
 Ren, Jicun, 528
 Riera, Víctor, 546
 Rim, Jeong Ah, 468
 Rudzka, Katarzyna, 489
 Sakaguchi, Satoshi, 486
 Senanayake, Kanthi, 474
 Sessler, Jonathan L., 540
 Steiner, Alexander, 459
 Suárez-Varela, José, 534
 Sundberg, Eric B., 477
 Szajna, Ewa, 489
 Takahashi, Isao, 471
 Thutewohl, Michael, 516
 Tradler, Thomas, 516
 Vishwakarma, Ram A., 453, 519
 Votta, Annamaria, 498
 Waldmann, Herbert, 516
 Wang, Pingshan, 465
 Wang, Shuai, 507
 Wang, Ximeng, 477
 Wärnmark, Kenneth, 549
 Watanabe, Nobuko, 483
 Willits, Deborah A., 487
 Winter, Rainer F., 510
 Xi, Lu, 492
 Xie, Songhai, 507
 Xu, Jin-Gou, 450
 Yamada, Masayo, 483
 Yan, Shirun, 507
 Yang, Wensheng, 492
 Yao, Jiannian, 492
 Young, Mark J., 447
 Yu, Chun-Wei, 450
 Zapf, Alexander, 431
 Zhan, Chuanlang, 462

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