

## Cover

The calculated transition states for the Diels–Alder reactions of singlet oxygen, nitroxyl and triazolinedione with butadiene and the ene reactions of the same three species with tetramethylethylene.

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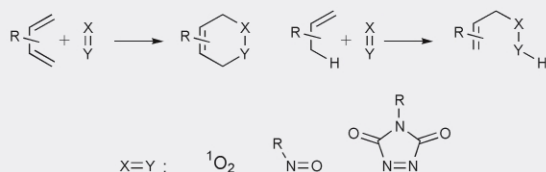
## contents

## FEATURE ARTICLE

1243

### Diels–Alder and ene reactions of singlet oxygen, nitroso compounds and triazolinediones: transition states and mechanisms from contemporary theory

Andrew G. Leach and K. N. Houk



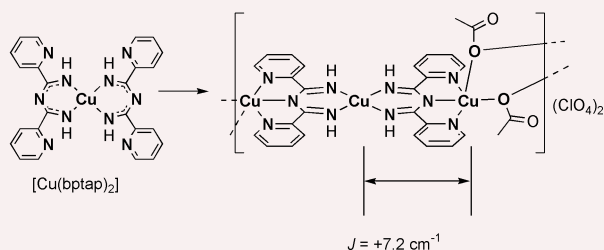
State of the art theoretical studies of the Diels–Alder and ene reactions of singlet oxygen, nitroso compounds and triazolinediones reveal mechanistic themes and subtle differences between these reactions.

## COMMUNICATIONS

1256

### Complexed bridging ligand, $\{\text{Cu}(\text{bptap})_2\}$ , as a ferromagnetic coupler

Takashi Kajiwara,\* Asako Kamiyama and Tasuku Ito\*

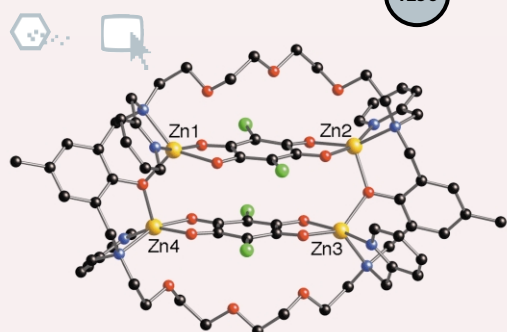


A novel complexed bridging ligand  $[\text{Cu}(\text{bptap})_2]$  which acts as a ferromagnetic coupler forms a one-dimensional chain consisting of tri-copper(II)  $[\text{Cu}_2\{\text{Cu}(\text{bptap})_2\}]^{4+}$  units.

1258

### Insertion of a strongly $\pi$ – $\pi$ stacked chloranilate pair into an $M_4$ arrangement preorganized within a large macrocyclic ligand ( $M = \text{Zn}^{2+}$ and $\text{Cu}^{2+}$ )

Atsushi Yoshino, Hideo Matsudaira, Eiji Asato,\* Masayuki Koikawa, Takuya Shiga, Masaaki Ohba and Hisashi Okawa

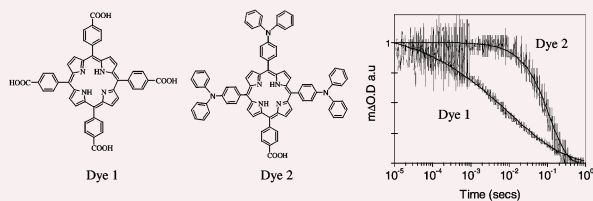


A strongly  $\pi$ – $\pi$  stacked chloranilate pair, inserted into four zinc(II) ions preorganized within a large macrocycle, is electrochemically reduced at  $E_{1/2} = -1.00 \text{ V}$  to produce a reasonably stable biradical species with  $T_{1/2} = 60 \text{ min}$  at  $25^\circ\text{C}$ .

1260

### Molecular control of recombination dynamics in dye sensitised nanocrystalline TiO<sub>2</sub> films

John N. Clifford, Gökhan Yahioğlu, Lionel R. Milgrom and James R. Durrant\*

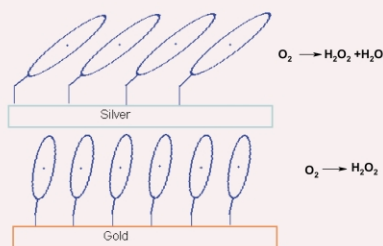


Modification of the structure of a dye shows a quantitative change in the recombination dynamics in a dye sensitised nanocrystalline TiO<sub>2</sub> film. These results are indicative of a transition from a trapping/detrapping limited to an interfacial limited recombination process.

1262

### Orientation dependent electrocatalysis using self-assembled molecular films

MallenaHalli P. Somashekarappa and Srinivasan Sampath\*

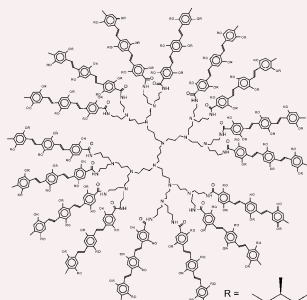


Orientation dependent electrocatalysis: a tetraamino derivative of a cobalt phthalocyanine yields different products depending on the orientation on the surface.

1264

### Formation and manipulation of supramolecular structures of oligo(*p*-phenylenevinylene) terminated poly(propylene imine) dendrimers

Albertus P. H. J. Schenning, Pascal Jonkheijm, Johan Hofkens, Steven De Feyter, Theodor Asavei, Mircea Cotlet, Frans C. De Schryver\* and E. W. Meijer\*

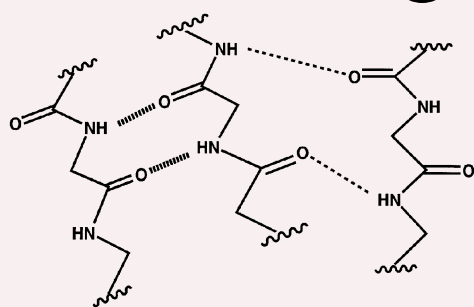


Poly(propylene imine) dendrimers modified with  $\pi$ -conjugated oligo(*p*-phenylenevinylene)s form spherical and rod-like aggregates that can be manipulated by optical tweezers.

1266

### Changes in motion vs. bonding in positively vs. negatively cooperative interactions

Dudley H. Williams,\* Christopher T. Calderone, Dominic P. O'Brien and Rosa Zerella

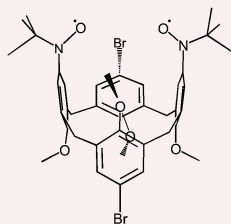


Negative cooperativity-structural loosening, benefit in entropy, cost in enthalpy.

1268

### Synthesis and reversible thermo-induced conformational transitions of a stable nitroxide biradical based on calix[4]arene

Qi Wang, Yong Li\* and Guo-shi Wu



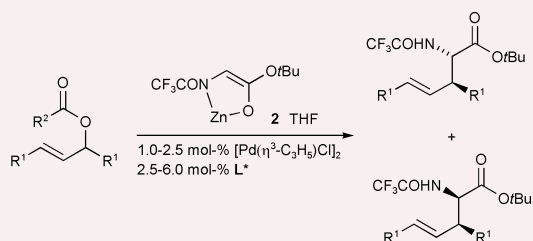
A stable paramagnetic calix[4]arene(III) bearing two nitroxide groups on the upper rim is synthesized, which exhibits a strong intramolecular spin-spin exchange interaction and is found to be able to undergo reversible conformational transitions upon heating.

1270

### Synthesis of amino acid derivatives *via* enantio- and diastereoselective Pd-catalyzed allylic substitutions with a non-stabilized enolate as nucleophile

Thomas D. Weiß, Günter Helmchen\* and Uli Kazmaier

Catalytic asymmetric syntheses of  $\alpha$ -amino acids *via* Pd-catalyzed asymmetric allylic substitutions with zinc enolates of glycine esters are described.

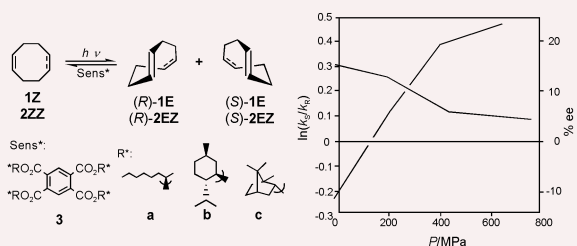


1272

### Discontinuous pressure effect upon enantiodifferentiating photosensitized isomerization of cyclooctene

Masayuki Kaneda, Sadayuki Asaoka, Haruhiko Ikeda, Tadashi Mori, Takehiko Wada and Yoshihisa Inoue\*

Hydrostatic pressure caused discontinuous changes in the ee of photoproduct upon photosensitized enantiodifferentiating isomerization, which is attributable to catastrophic conformational changes of chiral alkoxy carbonyl auxiliaries in benzenepolycarboxylate sensitizers.

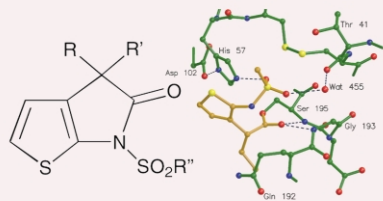


1274

### 5,5-Fused thiophene $\gamma$ -lactams as templates for serine protease inhibition

Marie E. Migaud, Rupert C. Wilmouth, Gary I. Mills, Gareth J. Wayne, Catherine Risley, Christopher Chambers, Simon J. F. Macdonald and Christopher J. Schofield\*

Kinetic, mass spectrometric and X-ray crystallographic analyses showed that novel 5,5-fused thiophene  $\gamma$ -lactams are potent inhibitors and acylating agents of human neutrophil and porcine pancreatic elastase.

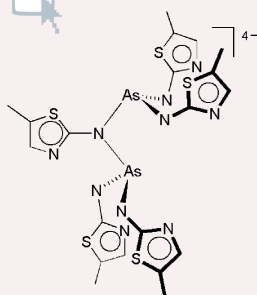


1276

### Synthesis of a deca-lithium cage containing an $[(RN)_2As(\mu-NR)As(NR)_2]^{4-}$ tetraanion; a homologue of group 15 trianions of the type $[E(NR)_3]^{3-}$

Andrew D. Bond, Felipe García, Katja Jantos, Gavin T. Lawson, Mary McPartlin and Dominic S. Wright\*

A deca-lithium cage is synthesised containing an  $[(RN)_2As(\mu-NR)As(NR)_2]^{4-}$  tetraanion, which represents a new type of multifunctional imido group 15 ligand framework (homologous with group 15 anions of the type  $[As(NR)_3]^{3-}$ ).

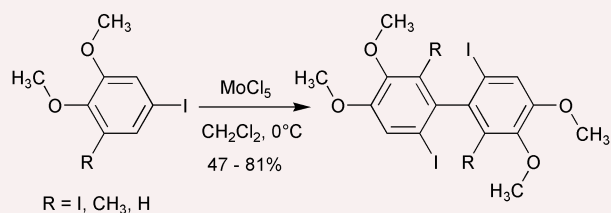


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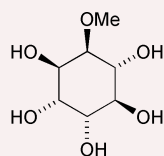
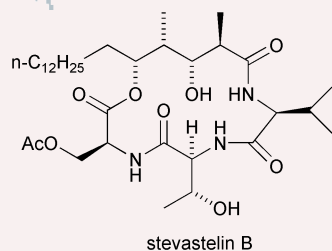
### Dehydrodimerization of iodobenzenes to iodinated biaryls

Siegfried R. Waldvogel,\* Eckhard Aits, Christiane Holst and Roland Fröhlich

The molybdenum pentachloride-mediated oxidative coupling of iodo-substituted electron rich benzenes without the loss of the iodo-substituents gives even access to 2,2',6,6'-tetraiodobiphenyl derivatives.



1280

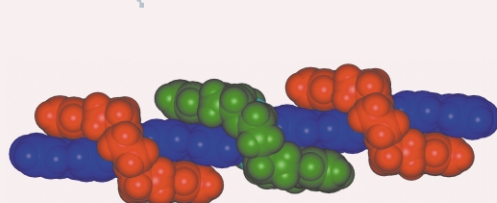


### Total synthesis of (–)-stevastelin B

Kazuo Kurosawa, Toshihiko Nagase and Noritaka Chida\*

The total synthesis of stevastelin B, a novel 15-membered cyclic depsipeptide starting from L-quebrachitol is described; this synthesis unambiguously confirmed the proposed structure of the natural product.

1282

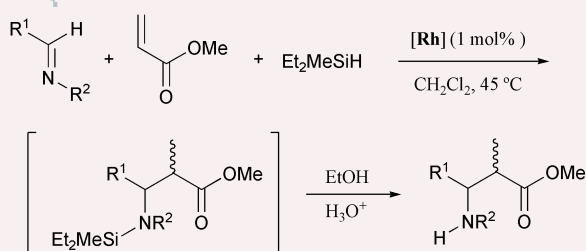


### Pseudo-polyrotaxanes based on a protonated version of the 1,2-bis(4,4'-bipyridinium)ethane–24-crown-8 ether motif

Jorge Tiburcio, Gregory J. E. Davidson and Stephen J. Loeb\*

A [2]pseudorotaxane is readily formed between dibenzo-24-crown-8 ether and diprotonated 1,2-bis(4,4'-bipyridinium)ethane. These sub-units are organized in the solid state to form unique non-covalent polymers containing mechanical linkages.

1284

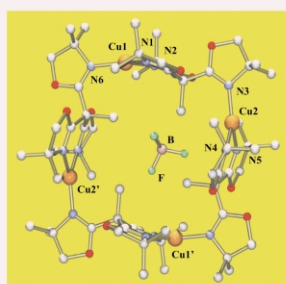


### Rhodium-catalyzed approach to Mannich-type products using aldimine, $\alpha,\beta$ -unsaturated ester, and hydrosilane

Takako Muraoka, Shin-ichi Kamiya, Isamu Matsuda\* and Kenji Itoh

A rhodium-catalyzed method for the synthesis of  $\beta$ -amino esters was accomplished in a one-pot procedure from aldimine,  $\alpha,\beta$ -unsaturated ester and hydrosilane.

1286

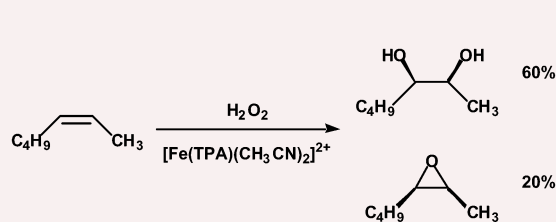


### Three 2-oxazolonyl rings on one quaternary carbon atom: preparation of a novel tripodal tris(oxazolonyl) ligand and the tetrameric molecular structure of its Cu<sup>I</sup> complex

Stéphane Bellemin-Lapponnaz and Lutz H. Gade\*

A novel tripodal ligand containing three 2-oxazolonyl rings on one quaternary carbon atom has been synthesized by coupling of a bisoxazoline and a monooxazoline derivative. Its copper complex, [Cu(trisox-Me<sub>2</sub>)](BF<sub>4</sub>), while monomeric in solution aggregates as a centrosymmetric tetramer in the solid state.

1288

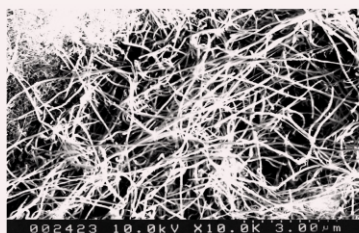


### High conversion of olefins to *cis*-diols by non-heme iron catalysts and H<sub>2</sub>O<sub>2</sub>

Ju Yeon Ryu, Jinheung Kim, Miquel Costas, Kui Chen, Wonwoo Nam\* and Lawrence Que Jr.\*

In our efforts to synthesise functional models of non-heme iron oxygenases, we have found the first iron complexes to catalyse the *cis*-dihydroxylation of olefins with high substrate-to-product conversion efficiency using HOOH as oxidant.

1290



### A novel precursor for synthesis of pure boron nitride nanotubes

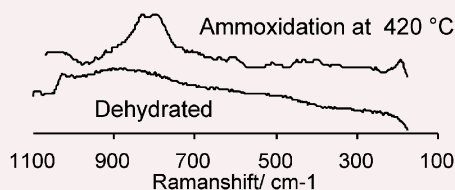
Chengchun Tang,\* Yoshio Bando, Tadao Sato and Keiji Kurashima

A mixture of B and MgO can be used to effectively synthesize bulk amounts of pure BN nanotubes and the Mg by-product is evaporated after reaction.

1292

### Operando Raman study of alumina-supported Sb–V–O catalyst during propane ammoxidation to acrylonitrile with on-line activity measurement

M. O. Guerrero-Pérez and M. A. Bañares\*



Operando Raman spectra during propane ammoxidation show partially reversible structural transformations of the active phases as a function of reaction environment.

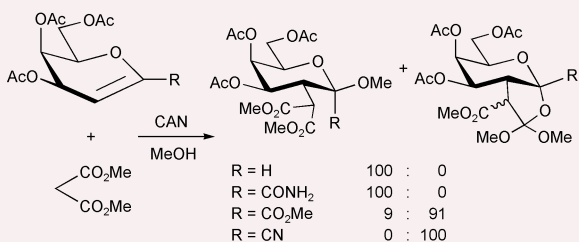
1294



### Addition of malonyl radicals to glycals with C-1 acceptor groups: remarkable influence of the substituents on the product distribution

Viktor Gyóllai, Dirk Schanzenbach, László Somsák\* and Torsten Linker\*

The ceric(IV) ammonium nitrate (CAN)-mediated radical addition of dimethyl malonate to glycals affords methyl glycosides and ortho esters as main products; the product distribution strongly depends on the substitution pattern at the 1-position.



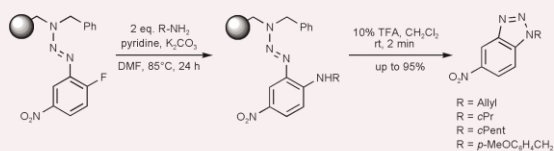
1296



### Solid supported fluoronitroaryl triazenes as immobilized and convertible Sanger reagents – synthesis and S<sub>N</sub>Ar reactions towards a novel preparation of 1-alkyl-5-nitro-1H-benzotriazoles

Matthias E. P. Lormann, Catherine H. Walker, Mazen Es-Sayed and Stefan Bräse\*

Synthesis of novel fluoronitroaryl triazenes in liquid phase and on solid support have been described; mild displacement of the fluoride ion with various nucleophiles provides access to substituted arenes which in turn can be cleaved to provide a unique access to 1-alkyl-5-nitro-1H-benzotriazoles.



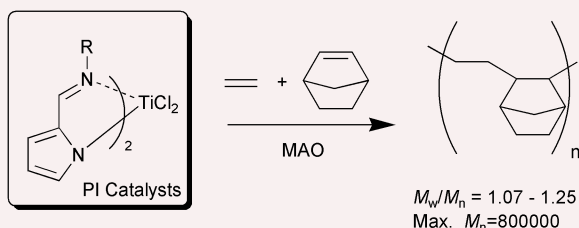
1298



### Living ethylene/norbornene copolymerisation catalyzed by titanium complexes having two pyrrolide-imine chelate ligands

Yasunori Yoshida, Junji Saito, Makoto Mitani, Yukihiko Takagi, Shigekazu Matsui, Sei-ichi Ishii, Takashi Nakano, Norio Kashiwa and Terunori Fujita\*

Titanium complexes possessing two pyrrolide-imine chelate ligands promote r.t. living ethylene/norbornene copolymerisation to form very high mol. wt. copolymers having extremely narrow mol. wt. distributions with high activities.



1300



### Synthesis of silver dendritic nanostructures protected by tetrathiafulvalene

Xiaqin Wang, Kensuke Naka,\* Hideaki Itoh, Sooyun Park and Yoshiki Chujo\*

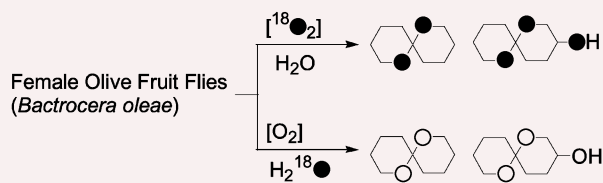
Silver dendritic nanostructures protected by tetrathiafulvalene (TTF) were synthesized *via* reduction of silver ions with TTF in acetonitrile.

1302

### Sex pheromone biosynthesis in the female olive fruit-fly. Double labelling from [<sup>18</sup>O<sub>2</sub>]-dioxygen into 1,7-dioxaspiro[5.5]undecane

Mary T. Fletcher, Basilis E. Mazomenos,\* John H. Georgakopoulos, Maria A. Konstantopoulou, Barry J. Wood, James J. De Voss\* and William Kitching\*

All oxygen atoms of 1,7-dioxaspiro[5.5]undecane are dioxygen derived. The proposed biosynthetic pathway emphasizes the centrality of monooxygenases, but recognises the complexity in the formation of the nine-carbon precursor.

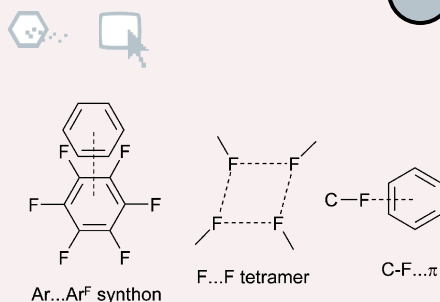


1304

### Interplay of phenyl–perfluorophenyl stacking, C–H···F, C–F···π and F···F interactions in some crystalline aromatic azines

Venu R. Vangala, Ashwini Nangia\* and Vincent M. Lynch

Different intermolecular interactions of fluorine are analysed in three closely related crystal structures.

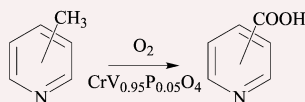


1306

### Crystalline CrV<sub>0.95</sub>P<sub>0.05</sub>O<sub>4</sub> catalyst for vapor-phase oxidation of picolines

Zhaoxia Song, Toshiyuki Matsushita, Tetsuya Shishido and Katsuomi Takehira\*

Picolines were selectively oxidized to the corresponding aldehydes and acids over crystalline CrV<sub>0.95</sub>P<sub>0.05</sub>O<sub>4</sub> catalyst assisted by the redox properties as well as the Brønsted acidity in the presence of water.

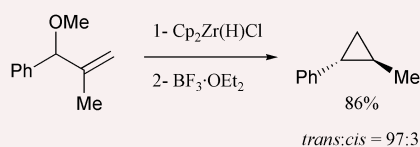


1308

### A one-pot access to cyclopropanes from allylic ethers *via* hydrozirconation–deoxygenative ring formation

Vincent Gandon and Jan Szymoniak\*

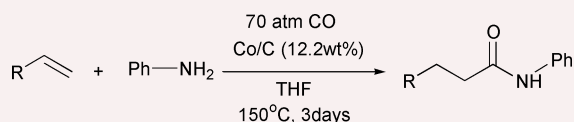
A synthetic method for the direct transformation of allylic ethers into mono-, di- and trisubstituted cyclopropanes is presented.



1310

**Catalytic one-pot synthesis of *N*-phenyl alkyl amides from alkene and aniline in the presence of cobalt on charcoal under carbon monoxide**

Sang Ick Lee, Seung Uk Son and Young Keun Chung\*

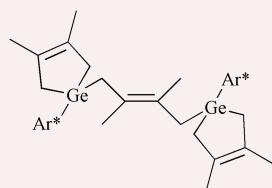


*N*-Phenyl alkyl amides were synthesized by the cobalt on charcoal-catalyzed one-pot reaction of alkene and aniline under carbon monoxide.

1312

**Formation of  $[\text{Ar}^*\text{Ge}\{\text{CH}_2\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}_2\}\text{CH}_2\text{C}(\text{Me})=]_2$  ( $\text{Ar}^* = \text{C}_6\text{H}_3\text{-2,6-Trip}_2$ ;  $\text{Trip} = \text{C}_6\text{H}_2\text{-2,4,6-}i\text{-Pr}_3$ ) via reaction of  $\text{Ar}^*\text{GeGeAr}^*$  with 2,3-dimethyl-1,3-butadiene: evidence for the existence of a germanium analogue of an alkyne**

Matthias Stender, Andrew D. Phillips and Philip P. Power\*

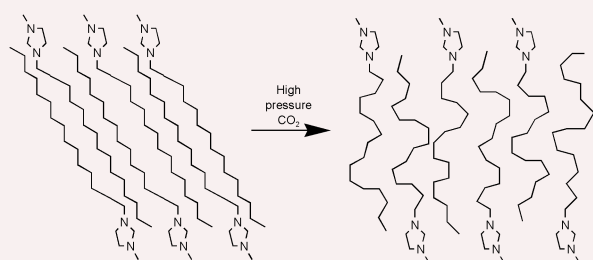


The reduction of  $\text{Ar}^*\text{GeCl}$  with one equivalent of potassium affords a germanium analogue of an alkyne  $\text{Ar}^*\text{GeGeAr}^*$  which reacts with dimethyl-1,3-butadiene to yield the structurally characterized compound  $[\text{Ar}^*\text{Ge}\{\text{CH}_2\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}_2\}\text{CH}_2\text{C}(\text{Me})=]_2$  **2**, illustrated opposite.

1314

**High-pressure  $\text{CO}_2$ -induced reduction of the melting temperature of ionic liquids**

Sergei G. Kazarian,\* Nikolaos Sakellarios and Charles M. Gordon\*

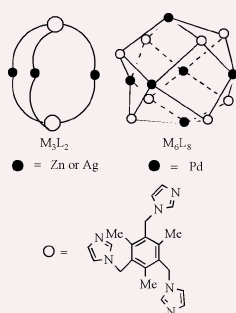


*In situ* ATR-IR spectroscopy has shown that high-pressure  $\text{CO}_2$  induces a reduction in the melting temperature of 1-hexadecyl-3-methylimidazolium hexafluorophosphate.

1316

**Assembly of supermolecular complexes from the tripodal ligand titmb: assembly of a large  $\text{M}_6\text{L}_8$  cage from 14 components**

Hong-Ke Liu\* and Xiaojun Tong



The synthesis and characterization of a  $\text{M}_6\text{L}_8$  cage complex  $[\text{Pd}_6(\text{titmb})_8]\text{Cl}_{12} \cdot 2\text{H}_2\text{O}$  (titmb = 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene), show the first example that the flexible tripodal ligand titmb can afford both  $\text{M}_3\text{L}_2$  and  $\text{M}_6\text{L}_8$  cage-like complexes when reacted with different metal ions.

## RETRACTION

1318

**New highly active chiral phosphapalladacycle catalysts. First isolation and characterization of a Pd(IV) intermediate**

Jean Michel Brunel, Marie-Hélène Hirlemann, Andreas Heumann and Gérard Buono

## CONFERENCE DIARY

x

Dates, venues and contact details of forthcoming events.

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\* Indicates the author for correspondence: see article for contact details.  
Supplementary crystallographic data are available: see article for further information.



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