

The cover shows virginiamycin M<sub>1</sub> bound to streptogramin acetyltransferase, as reported by Separovic and coworkers (p. 415).

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## Essay

### The Challenges with Substance Databases and Structure Search Engines

Helen Cooke, Damon D. Ridley

*Aust. J. Chem.* **2004**, *57*, 387–392.

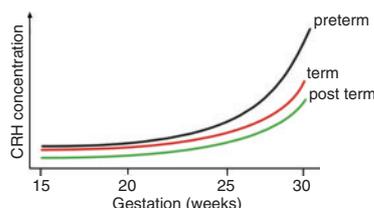
Databases of chemical structures have content often organized by specific valence bond structures; however this cannot represent many substances (such as polymers or salts) fully. Database compilers address this representation issue in different ways, and thus searching these databases demands some understanding of their organization and the associated search algorithms.

## Review

### Corticotrophin Releasing Hormone: Chemistry and Recent Developments

James Garner, Paul A. Keller,  
Adam McCluskey

*Aust. J. Chem.* **2004**, *57*, 393–407.



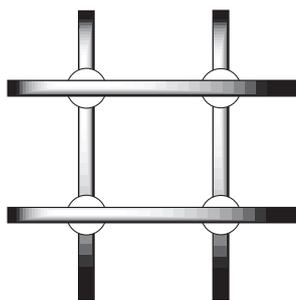
The occurrence of preterm birth comes at a large social and economic cost. The discovery of CRH, and exploitation of its biological action, is one of the most promising strategies in reducing its incidence. This review explores the development of peptidic and non-peptidic compounds as CRH<sub>1</sub> receptor agonists.

## Rapid Communications

### Self-Assembly of a Charge-Neutral Molecular Square

Mohammad Akbar Ali, Paul V. Bernhardt,  
Chong Lee Kiem, Aminul Huq Mirza

*Aust. J. Chem.* **2004**, *57*, 409–413.

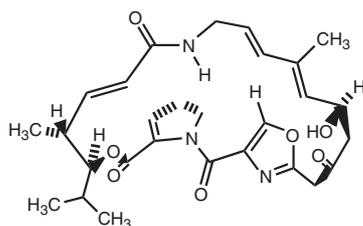


The X-ray crystal structure of a self-assembling, charge-neutral, tetracadmium(II) 2 × 2 grid is reported. <sup>1</sup>H NMR spectroscopy indicates that the solid-state structure is retained in methanol solution, and electrospray mass spectrometry indicates this is the dominant species in equilibrium with lower molecular weight oligomers.

### Difference in Conformation of Virginiamycin M<sub>1</sub> in Chloroform and Bound Form in the 50S Ribosome or Streptogramin Acetyltransferase

Jason Dang, B. Mikael Bergdahl,  
Frances Separovic, Robert T. C. Brownlee,  
Robert P. Metzger

*Aust. J. Chem.* **2004**, *57*, 415–418.



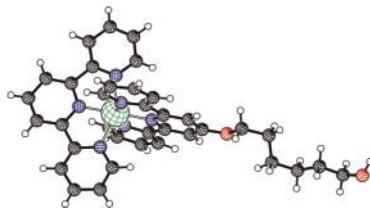
High-resolution NMR studies of the antibiotic virginiamycin M<sub>1</sub> establish that its conformation in solution is significantly different from the X-ray crystal structure of the form bound to the 50S ribosome and to the active site of a streptogramin acetyltransferase.

## Full Papers

### Terpyridine-Ruthenium Complexes as Building Blocks for New Metallo-Supramolecular Architectures

Harald Hofmeier, Philip R. Andres,  
Richard Hoogenboom,  
Eberhardt Herdtweck, Ulrich S. Schubert

*Aust. J. Chem.* **2004**, *57*, 419–426.

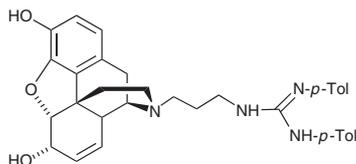


A series of asymmetric terpyridine-ruthenium(II) complexes has been prepared and characterized by various techniques including two-dimensional  $^1\text{H-NMR}$  spectroscopy and, in one particular case, X-ray structure analysis. Various functional groups have been introduced, which possess the potential for the construction of supramolecular architectures and polymers.

### Non-CNS Acting Opiates Bearing Guanidino Substituents

Kamani R. Subasinghe, W. Roy Jackson,  
Jacqui F. Young, Maria Papanastasiou,  
Bevyn Jarrott

*Aust. J. Chem.* **2004**, *57*, 427–438.

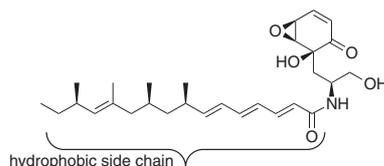


A range of modified opiates containing highly basic guanidine groups, which are protonated at body pH, has been prepared. Preliminary pharmacological evaluation shows that the compounds retain analgesic activity but are prevented from entering the central nervous system, thus eliminating many of the undesirable side effects associated with opiate use.

### Stereoselective Synthesis of the Hydrophobic Side Chain of Scyphostatin

Ryukichi Takagi, Shinjiro Tsuyumine,  
Hiroko Nishitani, Wataru Miyanaga,  
Katsuo Ohkata

*Aust. J. Chem.* **2004**, *57*, 439–447.



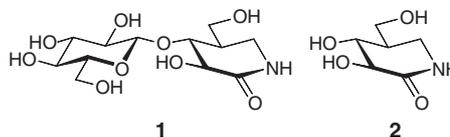
The synthesis of the hydrophobic side chain of the biphelic natural product scyphostatin involves enzymatic asymmetric acetylation of a *meso*-diol, a Negishi coupling reaction, and construction of the triene moiety by a Horner–Wadsworth–Emmons olefination. The differences in optical rotation values of the geometric isomers ( $2'E,4'E,6'E$ )-, ( $2'Z,4'E,6'E$ )-, ( $2'E,4'Z,6'E$ )-, and ( $2'E,4'E,6'Z$ )-ethyl ester are also described.

### The Synthesis of a D-Glucose-like Piperidin-2-one: Isofagomine Lactam

James M. Macdonald, Robert V. Stick

*Aust. J. Chem.* **2004**, *57*, 449–453.

Glycono lactams are enzyme inhibitors whose potency increases markedly when the N atom and C=O groups are in the pseudo-anomeric and C2 positions, respectively. As a precursor to D-glucosyl isofagomine lactam **1**, the authors report the synthesis of isofagomine lactam **2**. Hydrogenolysis, oxidation, and methanolysis of the 2,3-di-*O*-(*tert*-butyldimethylsilyl) derivative of benzyl 4-cyano-4-deoxy- $\alpha$ -D-arabinoside yielded a methyl ester. Reduction and deprotection then furnished **2**.

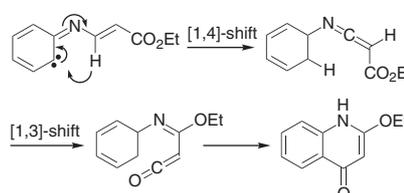


### Intramolecular Interactions in Carbenes Derived During the Pyrolysis of N-Alkenylisoxazolones

Matthew Cox, Michael Dixon,  
Troy Lister, Rolf H. Prager

*Aust. J. Chem.* **2004**, *57*, 455–460.

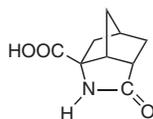
While the pyrolysis or photolysis of *N*-(1-alkenyl)isoxazolones generally proceeds through a carbene intermediate and gives pyrroles, alternate pathways were observed. These pathways may involve solvent capture by the triplet state, carbene rearrangement, or a [1,4]- then [1,3]- then cyclization cascade (as shown) to form a quinolone. This paper explores an alternate pathway involving the capture of the carbene by the carbonyl oxygen of esters and amides.



### Some Stereochemical Aspects of the Strecker Synthesis and the Bucherer–Bergs Reaction

Urs D. Wermuth, Ian D. Jenkins,  
Raymond C. Bott, Karl A. Byriel,  
Graham Smith

*Aust. J. Chem.* **2004**, *57*, 461–465.

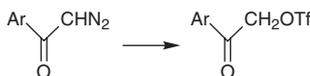


The unusually stable tricyclic lactam (shown) was prepared in attempting to prepare conformationally rigid analogues of the neurotransmitter L-glutamic acid by the Strecker or Bucherer–Bergs reaction. The stereochemistry obtained in the Strecker reaction was contrary to that expected, and it would appear that diastereoselectivity is controlled by the carboxylate group.

### Aracyl Triflates as Derivatizing Agents for Biological Betaines

D. Alan R. Happer, Colin M. Hayman,  
Malina K. Storer, Michael Lever

*Aust. J. Chem.* **2004**, *57*, 467–472.

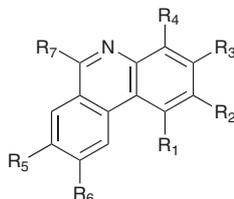


Many betaines play important roles in physiology and biochemistry. Thus, there is a demand for an accurate and reliable analytical method for detecting these compounds. The authors here synthesized a number of aracyl triflates, which were designed to enhance detection by the inclusion of a strong chromophore or fluorophore. These compounds were screened for their suitability for use in the analysis of betaine mixtures.

### The Action of Vanadium Oxytrifluoride on *N*-Arylbenzylamines—a Route to Some Phenanthridines

Andris J. Liepa, Roland N. Nearn,  
Denis M. J. Wright

*Aust. J. Chem.* **2004**, *57*, 473–482.

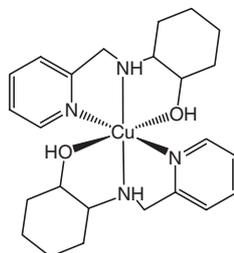


Phenanthridines—aza analogues of phenanthrenes—may be conveniently prepared from electron-rich *N*-arylbenzylamines and vanadium oxytrifluoride. Possible mechanisms of this reaction are proposed.

### Octahedral Complexes of a Mixed *N,N,O*-Donor Ligand *N-trans*-(2'-hydroxycyclohexyl)-2-aminomethylpyridine

Mark J. Robertson, Geoffrey A. Lawrance,  
Marcel Maeder, Peter Turner

*Aust. J. Chem.* **2004**, *57*, 483–490.

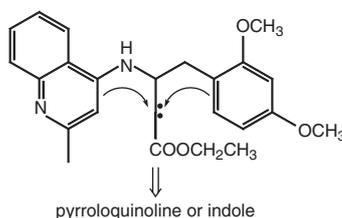


Synthesis and metal complexation of the unsymmetric mixed-donor ligand *N-trans*-(2'-hydroxycyclohexyl)-2-aminomethylpyridine **1** are described. The  $[\text{Cu} \cdot \mathbf{1}_2]^{2+}$ , shown, and  $[\text{Co} \cdot \mathbf{1} \cdot (\mathbf{1-H})]^{2+}$  complex ions were characterized as different geometric isomers by crystal structure analyses.

### The Role of Hydrogen Bonding in the Intramolecular Cyclization of Carbenes

David W. Jeffery, Troy Lister, Rolf H. Prager

*Aust. J. Chem.* **2004**, *57*, 491–496.

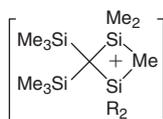


Photolysis of 3-aryl-4-ethoxycarbonyl-2-heteroarylisoxazolones (one shown) produces imidazopyridines or indoles. The intramolecular cyclization is apparently controlled by hydrogen bonding of the 3-NH group.

### The Reaction of Highly Hindered Silicon Halides with Nucleophiles

Janine K. Galligan, D. Alan R. Happer,  
Gareth R. S. Wilson

*Aust. J. Chem.* **2004**, *57*, 497–502.



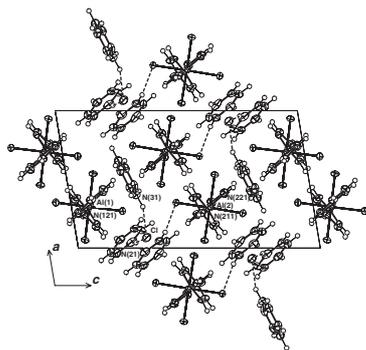
AgX-catalyzed nucleophilic displacement reactions of organosilicon iodides of type  $(\text{Me}_3\text{Si})_3\text{CSiR}_2\text{I}$  frequently yield two products,  $(\text{Me}_3\text{Si})_3\text{CSiR}_2\text{Y}$  and an isomer  $(\text{Me}_3\text{Si})_2\text{CSi}(\text{R}_2\text{Me})\text{SiMe}_2\text{Y}$ . The AgX- and HgX<sub>2</sub>-catalyzed solvolysis of  $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{Z}$  (Z = I, Br, H) in refluxing acetic acid is investigated here. The observed product distributions presumably arise from nucleophilic attack on a methyl-bridged cationic intermediate (shown).

## Short Communications

### The *trans*-[py<sub>2</sub>AlCl<sub>4</sub>]<sup>-</sup> ('py' = pyridine) Anion, Structurally Characterized in Two Pyridinium Salts

Peter C. Junk, Colin L. Raston,  
Brian W. Skelton, Allan H. White

*Aust. J. Chem.* **2004**, *57*, 503–506.

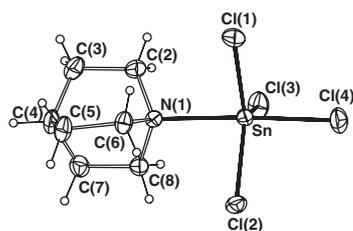


*Trans*-[py<sub>2</sub>AlCl<sub>4</sub>]<sup>-</sup> salts, as AlCl<sub>3</sub>·2HCl·4py and 2AlCl<sub>3</sub>·3HCl·7py (shown), have been structurally characterized, establishing a further member of the array [(py)<sub>n</sub>AlCl<sub>(6-n)</sub>]<sup>(n-3)±</sup> with 'octahedral' six-coordinate metal atom geometries.

### Coordination Complexes of Tin(IV) Chloride with Unidentate Nitrogen Bases

Warren A. Grigsby, Travis S. Morien,  
Colin L. Raston, Brian W. Skelton,  
Allan H. White

*Aust. J. Chem.* **2004**, *57*, 507–508.



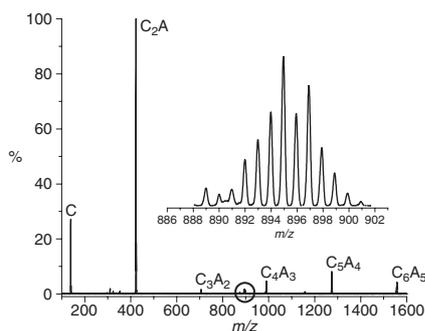
The reaction product of quinuclidine and tin(IV) chloride in toluene solution is, unusually, a five-coordinate neutral complex [qnSnCl<sub>4</sub>]. Sn–N occupies an axial site of a trigonal bipyramidal array.

## Focus

### Analysis of Ionic Liquids and Dissolved Species by Electrospray Ionization MS

Dongbin Zhao

*Aust. J. Chem.* **2004**, *57*, 509.



Electrospray ionization mass spectrometry is a useful tool for the detection and identification of many species, including transition metal based catalysts and ionic liquids, and ionic liquids are attracting increasing interest as solvents for multiphase catalysts. This article reports the characterization of a ruthenium catalyst immobilized in an ionic liquid (shown) and compares the ionic liquid synthesis by two different routes.

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