PART 1

Conference details
Abstracts for oral presentations
Delegate listing

Inorganic Division

11RACIC
Australian National University
6-11 February, 2000

The Royal Australian Chemical Institute

Inorganic Chemistry Division Conference

IC 2000 / 11 RACIC

6-11 February 2000

IC 2000

Australian National University

Canberra, Australian Capital Territory, Australia

Abstracts of

The Royal Australian Chemical Institute

Inorganic Chemistry Division Conference

IC2000/11RACIC

ANU, Canberra, ACT, Australia

6-11 February 2000

IC2000 Organizing Committee

Mark Humphrey (Chair)
Eric Wenger (Organizer, Bennett Symposium)
Bruce Wild
Rob Stranger

IC2000 Conference Abstracts Book

Mark Humphrey (Editor)
Marie Cifuentes
Nigel Lucas
Alison Turner

IC2000 Technical Support

Paul Gugger
Horst Neumann
Richard Webster

Acknowledgements

The IC2000 Organizing Committee wishes to thank the following sponsors for their generous support of IC2000:

Australian National University

CNRS (France)

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RACI ACT Branch

RACI Inorganic Chemistry Division

Research School of Chemistry

Royal Society (UK)

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General Information

The IC2000 component of the 11th RACI Convention will be held in the Manning Clark Centre Lecture Theatres 1-4, and Room 101 of the adjacent John Dedman Building. Convention Plenary Lectures will be delivered in Llewellyn Hall. Poster sessions for IC2000 will be held in the Karmel Room of the ANU Union Building. For those giving slide presentations, a slide preparation room is available (Room G052 of the Haydon Allen Building). Maps showing the Acton and Civic areas of Canberra (in which ANU is located), the ANU, and the Manning Clark Centre and environs (where the IC2000 papers will be delivered), are on the following pages.

Registration/Information Desk

The Registration/Information Desk will be located in the Foyer of the Manning Clark Centre. Messages can be left and retrieved at the Desk. There will be a Messages Board placed adjacent to the Desk. Fax or email messages to Division delegates can be left at:

+61 2 6249 0760 c/- Dr M.G. Humphrey, IC2000

or:

sent to Mark.Humphrey@anu.edu.au

Instructions to Speakers

All of the lecture theatres are equipped with 35 mm slide projectors, overhead projectors, microphone, remote slide control and projection screens. Those giving slide presentations should attend the slide preparation room (Room G052, Haydon Allen Building) in the tea/lunch break before their presentation. Carousels for slide projectors will be provided here. Speakers should ascertain that their slides are loaded correctly. Slide carousels should then be presented to the projectionist in your lecture theatre in this break before your session.

Instructions to Session Chairpersons

Session chairs are responsible for ascertaining that their session speakers are all in attendance(!), and ensuring that speakers restrict their presentations to their allocated timeframe (plenary lectures PL 40 min + 5 min questions, keynote lectures K 25 min + 5 min questions, oral presentations OP 15 min + 5 min questions). There are a large number of parallel sessions across the 11 RACIC programme, and firm adherence to the timetable will facilitate movement, not only between parallel inorganic sessions, but also between sessions of the Inorganic Division and those given by other Divisions of the RACI.

Instructions to Poster Presenters

Poster boards are 1 m wide x 2.1 m high. Attachments for fixing posters to boards will be available. Posters for the Monday poster session should be put up after the Monday afternoon oral presentation sessions, and should be removed at the end of the evening poster session. Similarly, posters for the Tuesday poster session should be put up after the Tuesday afternoon oral presentation sessions, and should be removed at the end of the poster session. It is essential to remove posters at the end of the poster sessions, as the poster boards will be removed at the end of these sessions. In the delegates list at the end of this abstracts book, **bold** entries indicate presenting authors, and non-bold entries indicate non-presenting co-authors.

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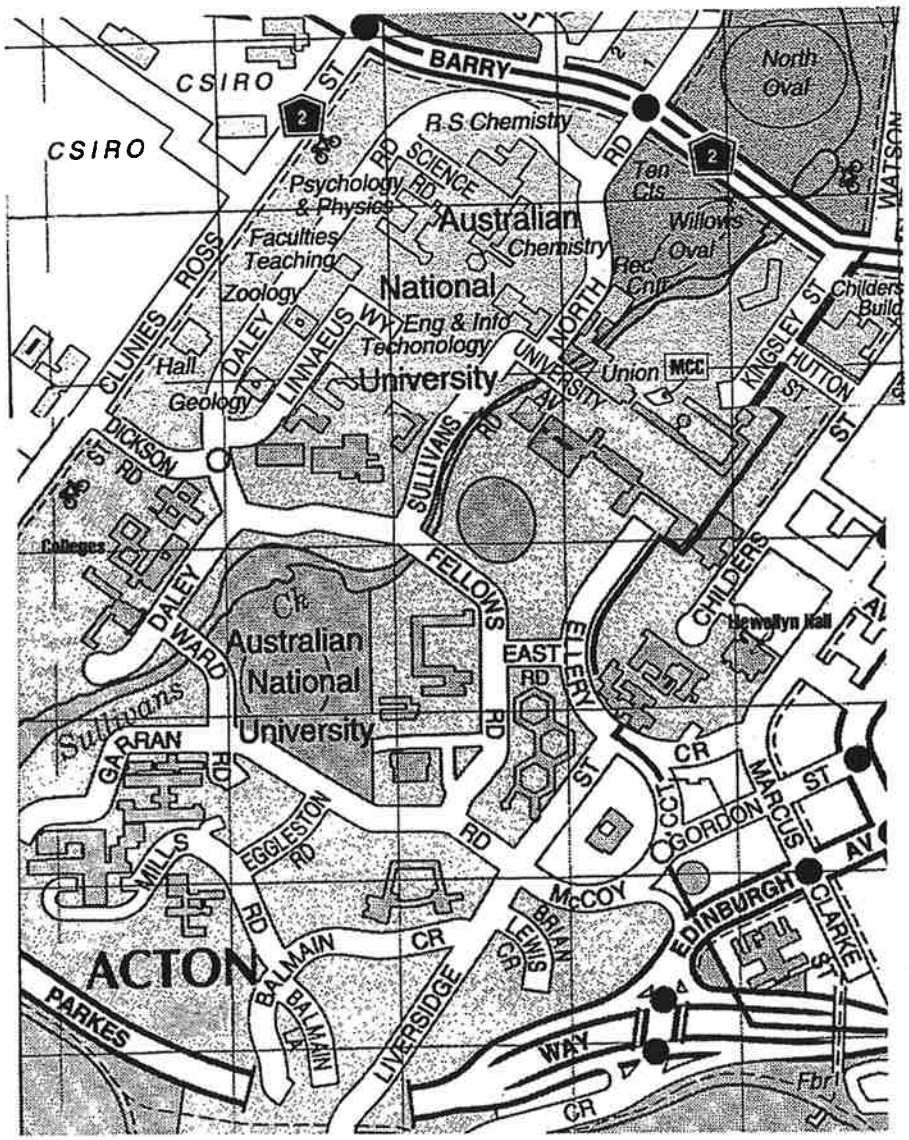
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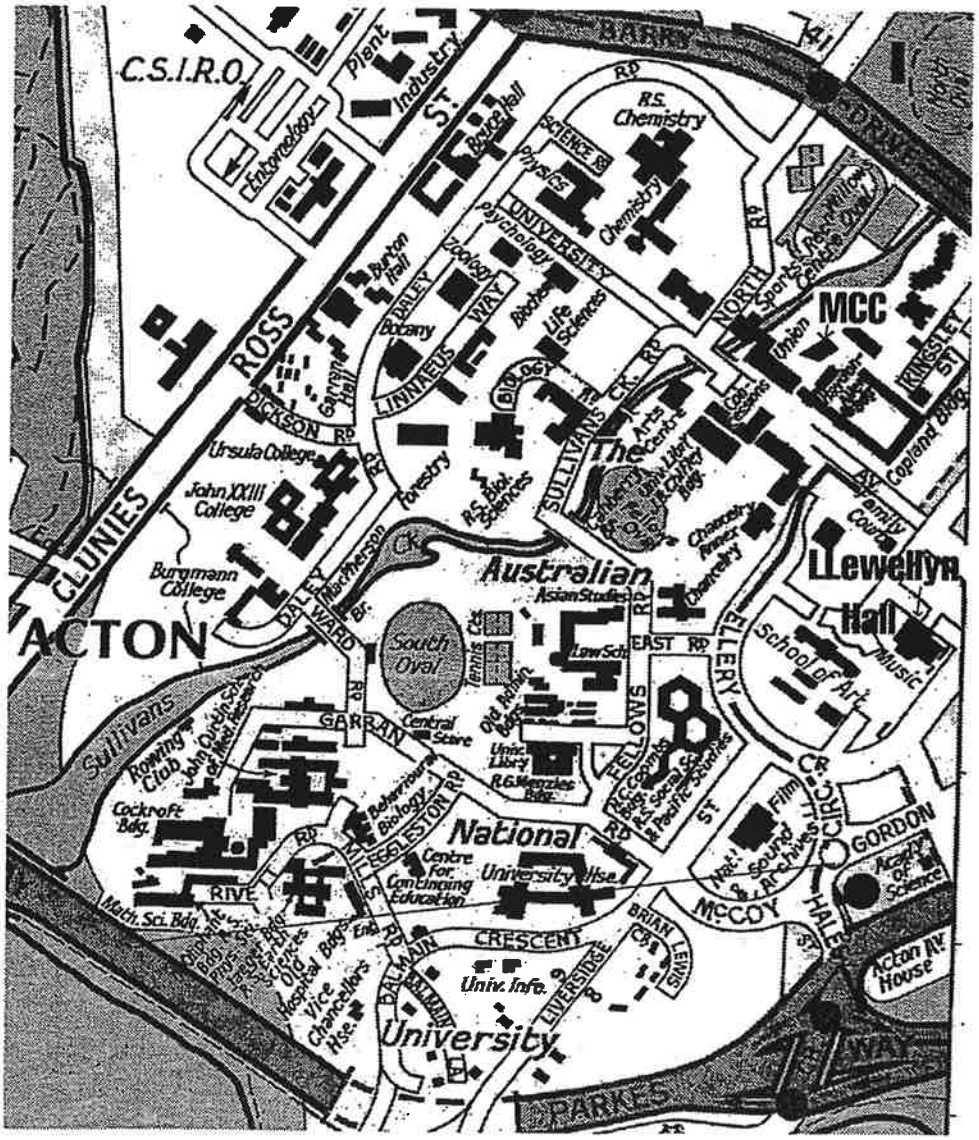
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Chancellery Annex
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Australian
Asian Studies
Law Sch.
EAST
ELLERY
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Music
Llewellyn Hall
MCC
NORTH
Sports Centre
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KINGSLEY
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Family Court
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Biochemistry Biology
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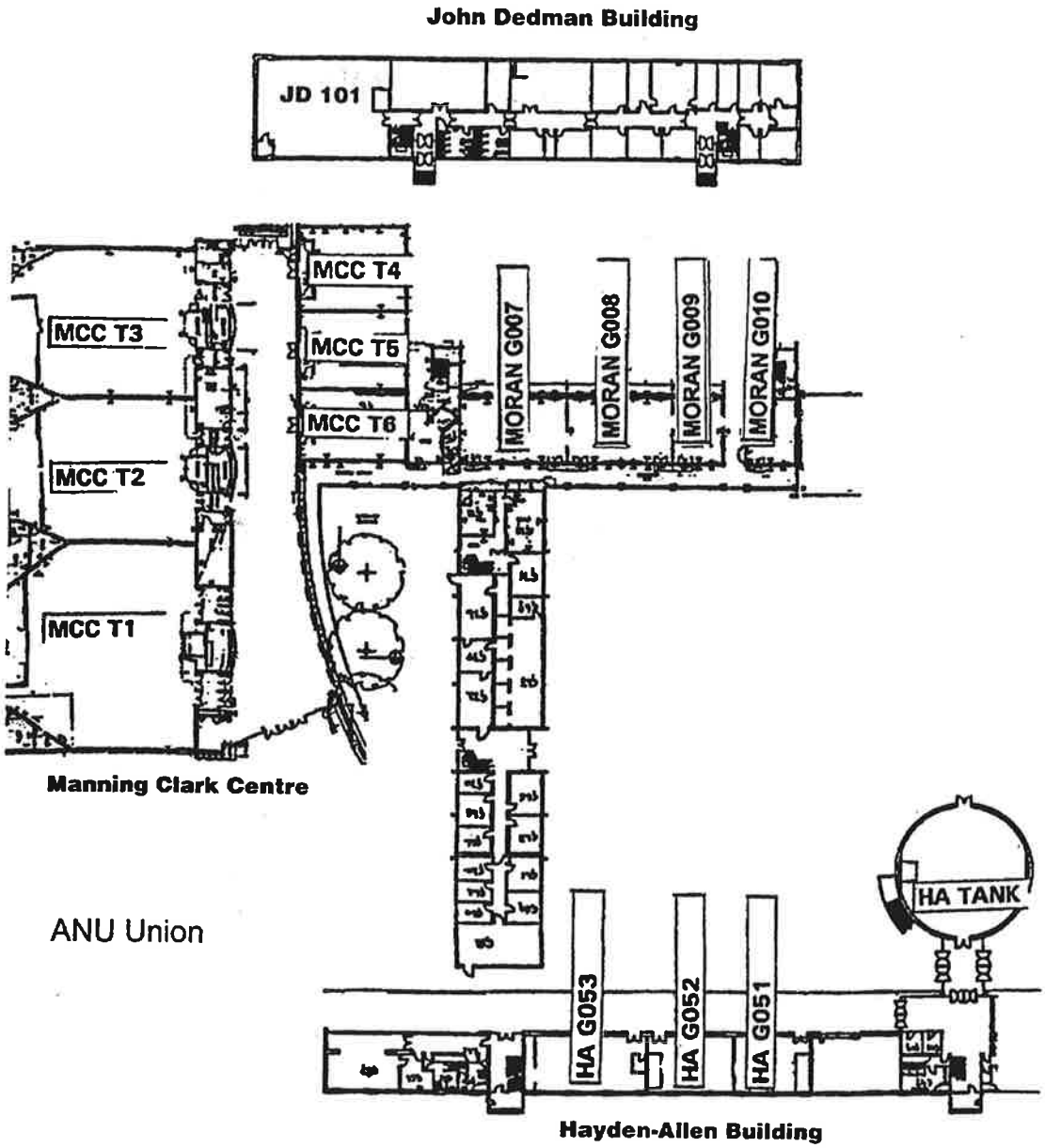


Lecture Theatre Locations

Concise IC2000 Conference Timetable

	SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY	
8:45					(MCC1) PL6 Bennett		8:45
9:00		(MCC1) PL1 Heck	(MCC1) PL3 Grubbs	(MCC3) PL5 Solomon		(MCC1) PL8 Mathey	9:00
9:15							9:15
9:30					OP27 Bosnich		9:30
9:45		K1 Murray	K4 Steel	K7 Young	OP28 Nakamura	K9 Williams	9:45
10:00							10:00
10:15		(MCC Foyer) Morning Tea					10:15
10:30							10:30
10:45		(MCC1) PL2 Hauser	(MCC1) PL4 Pfaltz	(MCC3) K8 Best	(MCC1) PL7 Maitlis	(MCC1) PL9 von Zelewsky	10:45
11:00							11:00
11:15				(MCC3) OP21 Hambley; (MCC4) OP24 Andrews			11:15
11:30		K2 Pace	K5 Schlesser	OP22 Wimmer; OP25 Brothers	OP29 Roper; OP30 Yamamoto; OP31 Griffith	K10 Lay; K11 Reed	11:30
11:45							11:45
12:00		OP1 Lüthi	OP11 Messerle	OP23 Colbran; OP26 Robinson			12:00
12:15							12:15
12:30		Lunch		Lunch			12:30
12:45							12:45
1:00		(MCC2) Discussion on RACI Divisions	(MCC2) Synchrotron Tutorial Freeman				1:00
1:15							1:15
1:30							1:30
1:45							1:45

2:00	(MCC Foyer) Registration	(LH) CP4 Selinger	(LH) CP6 Clark		(MCC3) OP32 Goh	(MCC4) OP37 Fisher	(MCC1) Burrows Lecture Bond	2:00
2:15					OP33 Mashima	OP38 Scott		2:15
2:30					OP34 Mays	OP39 Hartshorn		2:30
2:45					OP35 Pertici	OP40 Lincoln		2:45
3:00		CP5 Schmidbaur	CP7 Suter		OP36 Reger	OP41 Levina	Close of Meeting & Inorganic Division AGM	3:00
3:15								3:15
3:30								3:30
3:45		(MCC Foyer) Afternoon tea			Afternoon tea			3:45
4:00								4:00
4:15		(MCC3) K3 Raston	(MCC3) K6 Fackler		(MCC3) OP42 Komiya	(MCC4) OP46 Wedd		4:15
4:30					OP43 Leguna	OP47 Kepert		4:30
4:45		(MCC3) OP2 Wainwright / (JD101) OP5 Armstrong	OP15 Bruce		OP44 Mann	OP48 Schmid		4:45
5:00		OP3 Lewis / OP6 Baker	(MCC3) OP13 Rendina / (JD101) OP16 Gardiner		OP45 Vitulli	OP49 Nichols		5:00
5:15		OP4 Hardie / OP7 Keene	OP14 Dickson / OP17 Wright					5:15
5:30								5:30
5:45								5:45
6:00								6:00
6:15								6:15
6:30	(LH) Opening Ceremony							6:30
6:45	CP1 Cullen							6:45
7:00	CP2 Serjeantson				Conference Dinner			7:00
7:15								7:15
7:30	CP3 Williams	(MCC2) OP8 Ammala	(MCC2) OP18 Munk					7:30
7:45		OP9 Cross	OP19 Patterson					7:45
8:00	(Karmel) Mixer	OP10 Byrnes	OP20 Geue					8:00
8:15								8:15
8:30 on		(Karmel) Poster Session PM	(Karmel) Poster Session PT					8:30 on

IC2000 / 11 RACIC Programme

Key:

MCC	Manning Clark Centre
LH	Llewellyn Hall
Karmel	Karmel Room, 1st Floor, ANU Union Building
MCCx	Manning Clark Centre Lecture Theatre x
JD101	John Dedman Building, Room 101

Program for Sunday 6 February 2000

14:00 – 17:00	Registration (MCC Foyer)
17:00 - 18:30	**Dinner**
18:30 – 18:40	Opening ceremony (LH): R. JACKSON, President, RACI D. TERRELL, Vice-Chancellor, ANU
18:40 - 19:00	P. CULLEN, CRC for Freshwater Ecology, and Past President of the Federation of Australian Scientific and Technological Societies (Convention Plenary **CP1**) (LH)
19:00 - 19:20	S. SERJEANTSON, President, Federation of Australian Scientific and Technological Societies (Convention Plenary **CP2**) (LH)
19:20 – 19:50	N. WILLIAMS, CEO, Plastics and Chemical Industries Association (Convention Plenary **CP3**) (LH)
20:00 – 22:00	Mixer (Karmel)

Program for Monday 7 February 2000

	(JOINT INORGANIC/PHYSICAL) Materials Inorganic Chemistry (chair: M. G. Humphrey) (MCC1)
9:00 – 9:45	J. HECK, University of Hamburg, Germany (Plenary **PL1**) *Second Harmonic Generation and Two-Photon Fluorescence: Non-Linear Optical Properties of Mono- and Dinuclear Sandwich-Type Complexes*
9:45 – 10:15	K. S. MURRAY, Monash University (Keynote **K1**) *Molecule-Based Magnetic Materials Incorporating Metal Dicyanamides*
10:15 – 10:45	**Morning Tea** (MCC Foyer)
	(JOINT INORGANIC/PHYSICAL) Materials Inorganic Chemistry (chair: E. Krausz) (MCC1)
10:45 – 11:30	A. HAUSER, University of Geneva, Switzerland (Plenary **PL2**) *Cooperative Effects and Light-Induced Phenomena in Spin-Crossover Compounds*
11:30 – 12:00	R. J. PACE, Australian National University (Keynote **K2**) *The Gated Ion Channel Biosensor – a Functioning Nanomachine*
12:00 – 12:20	S. R. LUTHI, University of Queensland (Oral **OP1**) *Near-Infrared to Visible Upconversion in Rare-Earth Doped Halide Host Materials*
12:20 – 14:00	**Lunch**
13:00 - 13:45	Discussion group on the future of RACI divisional structures (chair: R. Jackson) (MCC2)

14:00 – 14:50	B. SELINGER, Australian National University (Convention Plenary **CP3**) (LH)	
14.50 - 15.40	H. SCHMIDBAUR, TU Munich, Germany (Convention Plenary **CP4**) (LH)	
15:40 – 16:10	**Afternoon Tea** (MCC Foyer)	
	(chair: I. G. Dance) (MCC3)	
16:10 – 16:40	C. L. RASTON, Monash University (Keynote **K3**) *Supramolecular Combinatorial Chemistry: Crystallisation of Superanion Capsules ('Russian Dolls') from Aqueous Media*	
	SESSION A (chair: I. G. Dance) (MCC3)	SESSION B (chair: P. Boyd) (JD101)
16:40 – 17:00	K. P. WAINWRIGHT, Flinders University (Oral **OP2**) *Metal Ion Activated Supramolecular Receptors*	R. S. ARMSTRONG, University of Sydney (Oral **OP5**) *XAFS Studies of Ruthenium and Osmium Dinitrogen Ammine Complexes*
17:00 – 17:20	G. R. LEWIS, University of New South Wales (Oral **OP3**) *The Supramolecular Chemistry of the Heavily Phenylated Ligands, $Ph_2P(CH_2)_nPPh_2$ (n = 1 to 4)*	M. V. BAKER, University of Western Australia (Oral **OP6**) *Using Copper Atoms to Bind Alkanephosphonates to Gold Surfaces*
17:20 – 17:40	M. J. HARDIE, Monash University (Oral **OP4**) *Crystal Engineering Host-Guest Systems: Assembly of Coordinate and H-Bonded Arrays with CTV and Inorganic Cage Molecules*	F. R. KEENE, James Cook University (Oral **OP7**) *Specific Anion Interactions with (Polypyridyl)ruthenium Complexes*
	Dinner	

Don Stranks Student Award talks
(chair: F.R. Keene) (MCC2)

19:30 – 19:50	P. AMMALA, Monash University (Oral **OP8**) *Reactions of "Basic" Fe(III) Carboxylates with Metal Alkoxides and Alcohols*
19:50 – 20:10	M. CROSS, University of Melbourne (Oral **OP9**) *Molecular Engineering at the Active Site of Rubredoxin*
20:10 – 20:30	M. J. BYRNES, Australian National University (Oral **OP10**) *Reactivity of cis-Bis(alkene)-bis(acetylacetonato)ruthenium(II) Complexes with Group 15 Donor Ligands*
20:30 – 22:30	POSTER SESSION (Karmel)

Program for Tuesday 8 February 2000

(JOINT ORGANIC/INORGANIC)
Organometallics in Synthesis
(chair: M. A. Bennett) (MCC1)

9:00 – 9:45 R. H. GRUBBS, California Institute of Technology, USA (Plenary **PL3**)
Design and Applications of Ruthenium Based Metathesis Catalysts

9:45 – 10:15 P. J. STEEL, University of Canterbury, New Zealand (Keynote **K4**)
New Metallosupramolecular Architectures

10:15 – 10:45 **Morning Tea** (MCC Foyer)

(JOINT ORGANIC/INORGANIC)
Organometallics in Synthesis
(Chair: S. Pyne) (MCC1)

10:45 – 11:30 A. PFALTZ, University of Basel, Switzerland (Plenary **PL4**)
Design of Chiral Ligands for Asymmetric Catalysis

(JOINT ORGANIC/INORGANIC)
Organometallics in Synthesis
(Chair: C. L. Raston) (MCC1)

11:30 – 12:00 C. H. SCHIESSER, University of Melbourne (RACI Organometallic Award address, Keynote **K5**)
Chirality Transfer – The Quest for Single-Enantiomer Outcomes in Free-Radical Chemistry

12:00 – 12:20 B. A. MESSERLE, University of New South Wales (Oral **OP11**)
Cationic Metal Catalysts with N-Donor Ligands

12:20 – 14:00	**Lunch**	
13:00 - 13:50	H. FREEMAN, University of Sydney (Informal Tutorial) (MCC2) *An Australian Synchrotron Light Source: Benefits and Costs for Australian Inorganic Chemistry*	
14:00 – 14:50	R. CLARK, University College London, UK (Convention Plenary **CP6**) (LH)	
14:50 – 15:40	U. SUTER, ETH Zurich, Switzerland (Convention Plenary **CP7**) (LH)	
15:40 – 16:10	**Afternoon Tea** (MCC Foyer)	
	(chair: W.G. Jackson) (MCC3)	
16:10 – 16:40	J. P. FACKLER, Texas A&M University, USA (Keynote **K6**) *Acid-base Behavior with Trinuclear Carbeniato Complexes of Gold(I). Intercalation by Cations and a Molecular Acid*	
16:40 – 17:00	M. I. BRUCE, University of Adelaide (Oral **OP15**) *Designs of Molecular Architecture Using Carbon Chains*	
	SESSION A (chair: W.G. Jackson) (MCC3)	SESSION B (chair: W. Roper) (JD101)
17:00 – 17:20	L. M. RENDINA, University of Adelaide (Oral **OP13**) *Non-Covalent Assembly of Multimeric Platinum Macrocycles*	M. G. GARDINER, University of Sydney (Oral **OP16**) *Polymer Supported N-Heterocyclic Carbene Complexes of Palladium: Well-Defined, Air-Stable and Recyclable, Heterogeneous Catalysts for the Heck Reaction*
17:20 – 17:40	R. S. DICKSON, Monash University (Oral **OP14**) *Cyclic Thioethers as Ligands – Some Surprising Attachments*	L. J. WRIGHT, University of Auckland, New Zealand (Oral **OP17**) *Functionalisation of σ-Aryl Complexes of Ruthenium and Osmium*

Dinner

Inorganic Division Committee meeting

Don Stranks Student Award talks
(chair: L. Gahan) (MCC2)

19:30 – 19:50	V. P. MUNK, University of Sydney (Oral **OP18**) *Steric Effects Can Induce Stereospecific Pt/DNA Binding*
19:50 – 20:10	B. T. PATTERSON, James Cook University (Oral **OP19**) *Chromatographic Separation of Stereoisomers of Helical and Bis(tridentate) Complex Systems*
20:10 – 20:30	J. P. GEUE, University of Adelaide (Oral **OP20**) *Fluorescent Chemosensors for the Detection of Metal Ions*
20:30 – 22:30	POSTER SESSION (Karmel)

Program for Wednesday 9 February 2000

(chair: A. Wedd) (MCC3)

9:00 – 9:45 E. I. SOLOMON, Stanford University, USA (Plenary **PL5**)
Geometric and Electronic Structure Contributions to Function in Non-Heme Iron Enzymes

9:45 – 10:15 C. G. YOUNG, University of Melbourne (Keynote **K7**)
Toward the First Model for the Molybdenum Hydroxylases

10:15 – 10:45 **Morning Tea** (MCC Foyer)

(chair: G.A. Heath) (MCC3)

10:45 – 11:15 S. P. BEST, University of Melbourne (Keynote **K8**)
Redox Activation of the Iron Molybdenum Cofactor of Nitrogenase

	SESSION A (chair: G.A. Heath) (MCC3)	SESSION B (chair: B.K. Nicholson) (MCC4)
11:20 – 11:40	T. W. HAMBLEY, University of Sydney (Oral **OP21**) *Sequence Selectivity of Cisplatin: 1,2- and 1,3-Intrastrand and 1,2-Interstrand Binding Kinetics of Cisplatin to DNA*	P. ANDREWS, Monash University (Oral **OP24**) *Homochiral Group 1 Amides: Synthesis, Structure and Aza-Allyl Formation*
11:40 – 12:00	F. WIMMER, University Brunei Darussalam, Brunei (Oral **OP22**) *The Influence of the Non-Leaving Groups on the Lipophilicity and the Pharmacological Properties of Some cis-Platinum(II) Complexes*	P. J. BROTHERS, University of Auckland, New Zealand (Oral **OP25**) *Formation of a Pendant-Arm Cyclam Ligand by Intramolecular Alkylation Reactions on a Cobalt(III) Complex: Coordination Chemistry and Photodecarboxylation to Give a Co-C-N Three-Membered Ring*

12:00 – 12:20	S. B. COLBRAN, University of New South Wales (Oral **OP23**) *Proton-Coupled Redox-Switchable Hemilability as a Basis for Conformational Proton-Pumping at a Transition Metal Centre*	B. H. ROBINSON, University of Otago, New Zealand (Oral **OP26**) *Synthesis and Vibrational Spectroscopy of New Switchable Organometallic Molecular Boxes*
12:20 – 14:00	**Lunch**	
	EXCURSION	

Program for Thursday 10 February 2000

SYMPOSIUM HONOURING MARTIN BENNETT
(chair: E. Wenger) (MCC1)

8:45 – 9:30 M. A. BENNETT, Australian National University (Plenary **PL6**)
Metal Complexes of Cyclic Alkynes: Retrospect and Prospect

9:30 – 9:50 B. BOSNICH, University of Chicago, USA (Oral **OP27**)
Bimetallic Reactivity

9:50 – 10:10 A. NAKAMURA, Toho University, Japan (Oral **OP28**)
Metal Enzyme Models Featuring Mono- and Di-thiolate Ligands. Importance of NH•••S Bonding for the Reactivity Control

10:15 – 10:45 **Morning Tea** (MCC Foyer)

SYMPOSIUM HONOURING MARTIN BENNETT
(chair: M. I. Bruce) (MCC1)

10:45 – 11:30 P. MAITLIS, University of Sheffield, UK (Plenary **PL7**)
Understanding Metal Catalysed Reactions: Organometallics to the Rescue

11:30 – 11:50 W. R. ROPER, University of Auckland, New Zealand (Oral **OP29**)
Boryl Complexes of Ruthenium and Osmium

11:50 – 12:10 A. YAMAMOTO, Waseda University, Japan (Oral **OP30**)
Development of Palladium-Catalyzed Halide-Free Catalytic Processes

12:10 – 12:30	W. P. GRIFFITH, Imperial College, UK (Oral **OP31**) *Oxometalates as Specific Organic Oxidation Catalysts*	
12:30 – 14:00	**Lunch**	
	SYMPOSIUM HONOURING MARTIN BENNETT SESSION A (chair: A. Canty) (MCC3)	SESSION B (chair: G.A. Lawrance) (MCC4)
14:00 – 14:20	L. Y. GOH, National University of Singapore, Singapore (Oral **OP32**) *My Small Contribution to Arene Ruthenium Chemistry – A Bennett Connection*	K. J. FISHER, University of New South Wales (Oral **OP37**) *Floating Inorganic Chemistry without a Solvent: Gas Phase Coordination Chemistry in a Mass Spectrometer*
14:20 – 14:40	K. MASHIMA, Osaka University, Japan (Oral **OP33**) *Linear Tetranuclear Pd-Mo-Mo-Pd Complexes with Palladium in Three Oxidation States Pd(0), Pd(I), and Pd(II)*	J. L. SCOTT, Monash University (Oral **OP38**) *Green Chemistry: Properties and Applications of Ionic Liquids*
14:40 – 15:00	M. J. MAYS, University of Cambridge, UK (Oral **OP34**) *Synthesis of New Sulfur-Containing Cyclic Ligands at Dinuclear Metal Centres*	R. M. HARTSHORN, University of Canterbury, New Zealand (Oral **OP39**) *Reactions of Iminodiacetate Bound to Cobalt(III) as a Didentate Ligand*
15:00 – 15:20	P. PERTICI, University of Pisa, Italy (Oral **OP35**) *Ruthenium(0) Complexes as Precursors of Homogeneous and Heterogeneous Catalysts*	S. F. LINCOLN, University of Adelaide (Oral **OP40**) *Aspects of Complexation and Supramolecular Chemistry in Metal Complexes of Pendant Arm Polyazamacrocycles*
15:20 – 15:40	D. L. REGER, University of South Carolina, USA (Oral **OP36**) *Tris(pyrazolyl)methane Ligands: Syntheses of Iron(II) Complexes with Unusual Magnetic Properties*	A. LEVINA, University of Sydney (Oral **OP41**) *Stabilization of Chromium(V/IV) by a Naturally Occurring Ligand, Quinic Acid*
15:40 – 16:10	**Afternoon Tea** (MCC Foyer)	

	SYMPOSIUM HONOURING MARTIN BENNETT SESSION A (chair: T. Appleton) (MCC3)	SESSION B (chair: L. Spiccia) (MCC4)
16:10 – 16:30	S. KOMIYA, Tokyo University of Agriculture and Technology, Japan (Oral **OP42**) *Carbon-Heteroatom Bond Activation on Ruthenium(0) Complexes*	A. G. WEDD, University of Melbourne (Oral **OP46**) *The New Classic Heteropoly Anion, $[S_2W_{18}O_{62}]^{4-}$*
16:30 – 16:50	M. LAGUNA, University of Zaragoza, Spain (Oral **OP43**) *Sensors for VOC's Based on Organogold Thiolate Complexes*	C. J. KEPERT, University of Sydney (Oral **OP47**) *Porous, Chiral Molecular Framework Materials – Crystal and Guest-Exchange Chemistry*
16:50 – 17:10	B. E. MANN, University of Sheffield, UK (Oral **OP44**) *The Fluxionality of $[Fe_3(CO)_{12}]$ and its Derivatives*	S. SCHMID, Australian National University (Oral **OP48**) *$Ca_7Nb_6Zr_7O_{36}$ - Synthesis and Structure Refinement of a New Anion-Deficient, Fluorite-Related Superstructure Phase*
17:10 – 17:30	G. VITULLI, University of Pisa, Italy (Oral **OP45**) *Advances in the Metal Vapour Derived Catalysts*	P. J. NICHOLS, Monash University (Oral **OP49**) *Confinement of $[(H_2O)_2 \cap$ (18-Crown-6)] in a Disc Shaped Cavity Lined with Six Nickel(II) Macrocycle Dimers*
19:00 – late	**Conference Dinner (Parliament House)**	

Program for Friday 11 February 2000

	(chair: S.B. Wild) (MCC1)
9:00 – 9:45	F. MATHEY, CNRS Palaiseau, France (Plenary **PL8**) *Advances in the Chemistry of Aromatic Phosphorus Ligands*
9:45 – 10:15	A. F. WILLIAMS, University of Geneva, Switzerland (Keynote **K9**) *Helical Complexes – More than Pretty Structures*
10:15 – 10:45	**Morning Tea** (MCC Foyer)
	(chair: L. Lindoy) (MCC3)
10:45 – 11:30	A. VON ZELEWSKY, University of Fribourg, Switzerland (Plenary **PL9**) *Metallic Elements as Chiral Centers in Molecules*
11:30 – 12:00	P. A. LAY, University of Sydney (Keynote **K10**) *Structure Determinations of Small Molecule Binding to Heme Proteins Using EXAFS*
12:00 – 12:30	C. A. REED, UC Riverside, USA (Keynote **K11**) *Super Anions and Superacids*
12:30 – 14:00	**Lunch**
14:00 – 15:00	(chair: C.L. Raston) (MCC1)
	A. M. BOND, Monash University (**Burrows Lecture**) *Broadening the Horizons of Inorganic Electrochemistry*
15:00 – 15:45	Inorganic Division AGM and close of meeting (MCC1)

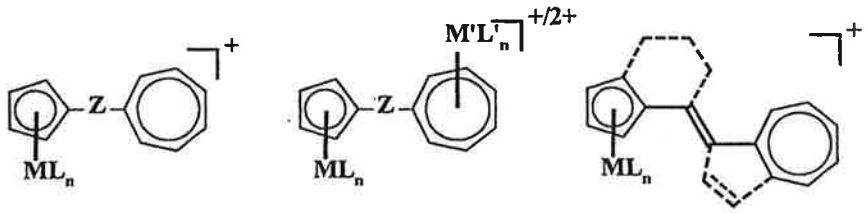
PLENARY LECTURES

Second Harmonic Generation and Two-Photon Fluorescence: Nonlinear Optical Properties of Mono- and Dinuclear Sandwich-Type Complexes

Jürgen Heck

Institut für Anorganische und Angewandte Chemie, Universität Hamburg
Martin-Luther-King-Platz 6, D-20146 Hamburg

Currently, the most important class of nonlinear optical (NLO) compounds providing second harmonic generation (SHG) are comprised of electron donating and accepting groups which are electronically coupled. Organometallic donating and accepting groups exhibit interesting features which allow a tuning or even switching of the NLO properties. In our research we are evaluating the SHG of dipolar mono- and bimetallic sandwich-like complexes composed of sesquifulvalenes and metal-ligand fragments ML_n and $M'L'_n$ stabilizing the aromatic units of the sesquifulvalenes (I, II). The aromatic units are separated by π-linkers Z, such as olefins and thiophenes, which allow electronic communication between the donor and acceptor moiety. Additionally corresponding sequifulvalene complexes are studied, wherein the donor or acceptor moiety or both are fixed in the plane of the π-bridge (III).



I II III

Electrochemical and UV-vis spectroscopic studies indicate a distinct mutual influence of the metallocene donor and the tropylium acceptor. The first hyperpolarizability β has been experimentally determined by means of hyper-Rayleigh scattering. These studies demonstrate that most of the ferrocenyl derivatives fluoresce in the region of the SHG due to two-photon absorption whereas the ruthenium congeners show pure SHG. The obtained β-values are large, and can be partly explained by resonance enhancement.

Cooperative effects and light-induced phenomena in spin-crossover compounds

PL 2

Andreas Hauser, Roland Hinek, Jelena Jeftic, Harald Romstedt, Sabine Schenker, Regula Sieber, Hartmut Spiering and Mohamed Zerara

Département de chimie physique, Université de Genève, 30 quai Ernest-Ansermet, 1211 Geneva, Switzerland. e-mail: andreas.hauser@chiphy.unige.ch

The phenomenon of spin-crossover for octahedral transition metal complexes with a d^4 to d^7 electron configuration, having two low-lying electronic states of different spin multiplicities within thermal energies of each other, is well documented. For Fe(II) spin-crossover compounds in particular, the entropy-driven transition from the $^1A_1$ low-spin state at low temperatures to the $^5T_2$ high-spin state at elevated temperatures is accompanied by an increase in metal-ligand bond lengths of ~0.2 Å and a concomitant large increase in volume. The resulting elastic interactions can be thought of as being made up of two contributions: a long-range part corresponding to a changing internal pressure, and a short-range part depending upon specific nearest neighbour interactions. The internal pressure change is proportional to the macroscopic expansion and contraction of the crystal as it is cycled through the spin transition, resulting in a positive feedback. Thus an increasing low-spin fraction results in an increasing internal pressure, which, in turn, further destabilises the high-spin state. Thermal transition curves in neat spin-crossover compounds are thus invariably much steeper than in diluted mixed crystals and may even show hysteresis behaviour. Secondary effects of the elastic interactions include crystallographic phase transitions, inhomogeneous distributions of zero-point energies, and anomalies such as incomplete transitions and steps in the transition curve. The latter are thought to be due to comparatively strong nearest neighbour interactions, which in contrast to the long-range interactions may favour the formation of chess board like patterns.

In addition to the thermal spin transition, a light-induced population of the high-spin state at temperatures well below the thermal transition temperature can be achieved. At $T \leq 20$ K, the lifetimes of such high-spin states can be as long as several days. As a result of the elastic interactions, the high-spin→low-spin relaxation following the light-induced population of the high-spin state is self-accelerating. Conversely, a light-induced bistability may be induced in the case of compounds with initially a high-spin ground state and the potential for a light-induced population of the low-spin state. For such a compound, the high-spin state may become destabilised to such an extent by the increasing internal pressure that the low-spin state may in fact become the molecular ground state above some critical light-induced low-spin fraction.

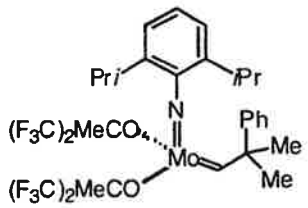
The concept of internal pressure for the description of cooperative effects in a mean field approach has some physical significance and can be compared to the effect of external hydrostatic pressure on both the thermal spin transition as well as the high-spin→low-spin relaxation. At low temperatures the latter is accelerated by one order of magnitude by an external pressure of 1 kbar. The internal pressure can also be varied by doping the spin-crossover complex into inert host matrices with cavities of varying size. A most striking example is provided by the incorporation of $[Co(bpy)_3]^{2+}$ into an oxalate network structure. In the very restricted cavities of such a network the classic d^7 high-spin complex turns into a spin-crossover complex.

The above mentioned properties of spin-crossover compounds provide the scientific background for their application as advanced materials in optical data processing which is currently being discussed by various research groups around the world.

Design and Applications of Ruthenium Based Metathesis Catalysts

Robert H. Grubbs, Matthias Scholl, Tina M. Trnka, John P. Morgan
California Institute of Technology

Over the past few years the olefin metathesis reaction has emerged as a powerful tool for the formation of C-C bonds in complex molecules. Ring closing metathesis (RCM) has seen the broadest applications with cross metathesis (XMET) finding an increasing role. Key to these advances is the availability of well-defined alkylidene-metal complexes for this transformation that include the alkoxy imido molybdenum complex **1** [1] and the benzylidene ruthenium complex **2**.[2] The molybdenum complex **1** is more reactive towards a broad range of substrates with many steric or electronic variations;[3] however, it also suffers from high sensitivity to air and moisture and decomposition upon storage. To increase the activity and selectivity of the ruthenium family, new derivatives of **2** have been prepared. These derivatives of **2** include bidentate salicylaldimine ruthenium complexes, [4] binuclear ruthenium complexes,[5] and ruthenium complexes with a family of imidazolinylidene ligands.[6] These designs are based on the mechanistic studies that demonstrated that the activity of the system was related to the large cone angle and basicity of the cyclohexylphosphine.[7] Continued improvements based on these mechanistic observations have led to a new family of functional group tolerant ruthenium catalysts with activity and efficiency superior to that of **1**.[8]



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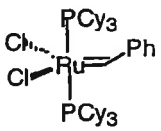

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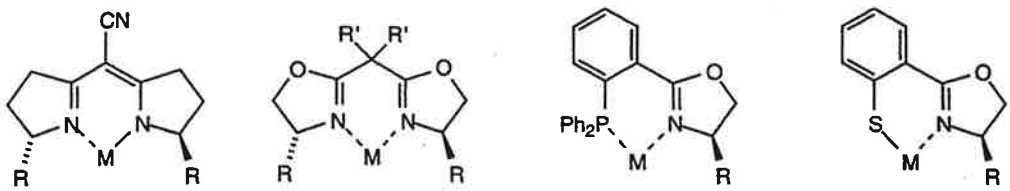
DESIGN OF CHIRAL LIGANDS FOR ASYMMETRIC CATALYSIS

Andreas Pfaltz

Department of Chemistry, University of Basel
St. Johanns-Ring 19, CH-4056 Basel (Switzerland)
e-mail: Andreas.Pfaltz@unibas.ch

During the last years we have developed several new classes of chiral ligands derived from oxazolines and other *N*-heterocycles [1]. In this lecture the properties and various applications of these ligands in asymmetric catalysis are presented.

C_2-Symmetric bisoxazolines **2**, which have evolved from our work on chiral semicorrins **1**, are versatile ligands for a wide spectrum of metal-catalyzed reactions [2]. Copper complexes **2** (M = Cu^I), for example, are efficient catalysts for enantioselective cyclopropanation [1, 2] or allylic oxidation of olefins [3]. For a number of metal-catalyzed processes, non-symmetric phosphino-oxazolines [4] or mercapto-oxazolines [5] have proven to be superior to C_2-symmetric bidentate nitrogen ligands. Enantioselective reactions based on catalysts of the type **3** (M = Pd, W, Ir) or **4** (M = Cu^I) include allylic substitution [1], Heck reactions [6], hydrogenation [7], and 1,4-addition of Grignard reagents to enones [5].



1 **2** **3** **4**

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PL 5

Geometric and Electronic Structure Contributions to Function in Non-Heme Iron Enzymes

Edward I. Solomon
Department of Chemistry, Stanford University, Stanford, CA 94305
e-mail: edward.solomon@stanford.edu

Non-heme iron active sites are found in a wide range of enzymes which perform different biological functions requiring dioxygen. These reactions often involve dioxygen activation by a ferrous active site which is generally difficult to study with most spectroscopic methods. A new spectroscopic methodology has been developed utilizing variable temperature, variable field magnetic circular dichroism (VTVH MCD) which enables one to obtain detailed insight into the geometric and electronic structure of the non-heme ferrous active site and probe its reaction mechanism on a molecular level. This spectroscopic methodology will be presented and applied to a number of key mononuclear non-heme iron enzymes leading to a general mechanistic strategy for O_2 activation. These studies will then be extended to consider the new features present in the binuclear non-heme iron enzymes and applied to 1) understand the mechanism of the two electron/coupled proton reaction of dioxygen binding to hemerythrin, and 2) structure/function correlations over stearoyl-ACP Δ^9 desaturase, ribonucleotide reductase and methane monooxygenase. Electronic structure/reactivity correlations for O_2 activation by non-heme iron enzymes will also be considered.

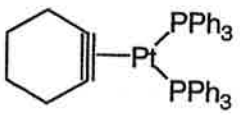
Metal Complexes of Cyclic Alkynes: Retrospect and Prospect

PL 6

Martin A. Bennett

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia, (email: bennett@rsc.anu.edu.au)

Recurrent themes in organometallic and coordination chemistry are the modification of ligand reactivity and the stabilization of short-lived or unusual groups at transition metal centres. Complexes of cyclohexyne and benzyne with d^{10} transition elements, such as **1** and **2**, have provided not only the first examples of this class of compound but also a rich source both of unexpected chemistry and still unsolved problems. In this lecture I discuss some of these developments as they have occurred over the last thirty years.



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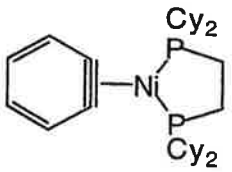


2

(Cy = cyclohexyl)

PL 7

Understanding metal catalysed reactions: Organometallics to the rescue

Peter Maitlis

Depertment of Chemistry
University of Sheffield, Sheffield, S3 7HF, UK

Abstract

Organic reactions catalysed by metals, either homogeneously as soluble complexes in solution, or heterogeneously, by metal surfaces, involve metal-carbon bonds, in other words, organometallic species. Catalytic cycles can conveniently be considered to be composed of a series of stoicheiometric reactions. It is therefore now possible to understand catalytic processes qualitatively and even quantitatively by applying quite basic principles of organo-transition metal chemistry.

The lecture will be illustrated by current examples from the work of the Sheffield group.

Advances in the chemistry of aromatic phosphorus ligands

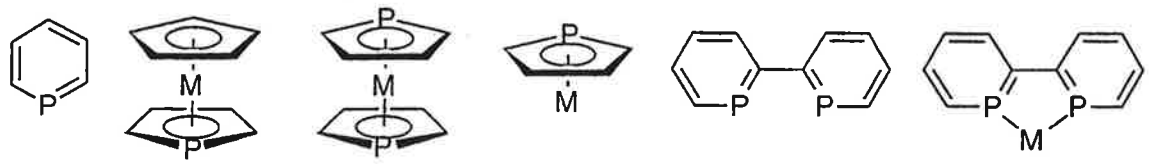
François Mathey, Duncan Carmichael, Pascal Le Floch

Laboratoire "Hétéroéléments et Coordination" UMR 7653 CNRS, DCPH, Ecole Polytechnique,

91128 Palaiseau cedex, France

e-mail: francois.mathey@polytechnique.fr

Among aromatic carbon-phosphorus heterocycles, two types, namely the phosphinines (I) and the phosphametallocenes (II - IV) display favourable characteristics for possible use in coordination chemistry and catalysis. Indeed, they are readily available with a variety of substitution patterns and they are quite stable. In all these species, the in-plane sp^2-phosphorus lone pair is low in energy and the LUMO is highly localized at phosphorus. Thus, they behave as weak σ-donors and strong π-acceptors. In this report, we shall describe our latest advances in the field. This includes a versatile synthesis of 2,2'-biphosphinines (V) and a description of their coordination chemistry. The reduction of 2,2'-biphosphinines gives a dianion whose reaction with MX_2 gives the chelates (VI). Several homoleptic complexes have thus been made. Some parallel can be drawn with the corresponding metal carbonyls, although the geometries are different in most cases. In a second part, we shall describe our results concerning the synthesis of phosphametallocenes derived from the main group elements and some paramagnetic 19- and 20-electron species. Preliminary results on the use of phosphametallocenes in homogeneous catalysis will serve as a conclusion.



(I) (II) (III) (IV) (V) (VI)

Bibliography:

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Metallic Elements as Chiral Centers in Molecules

PL 9

Alexander von Zelewsky

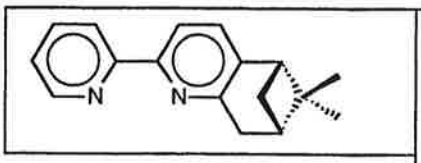
Institute of Inorganic Chemistry, University of Fribourg, Perolles, CH-1700 Fribourg (Switzerland)
e-mail: Alexander.vonzelewsky@unifr.ch

The carbon atom as chiral center has been a subject of great importance in many fields of organic chemistry, especially with naturally occurring compounds. Accordingly, synthetic organic chemists dispose of many efficient methods of stereoselective synthesis, where carbon atoms are introduced as chiral centers into a molecule with preference for one of the two possible absolute configurations. In most cases this is achieved through diastereo-selective reactions.

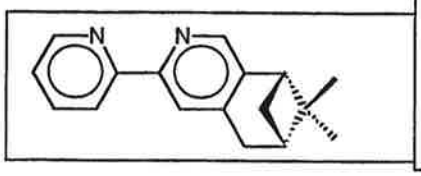
Although metal centers have been known to have the possibility to occur as centers of chirality since the first resolution of a racemate of a coordination compound by Alfred Werner, [1] their diastereoselective syntheses were only sporadically reported. The development of the field since the first mentioning of a diastereoselecetive synthesis by Smirnoff has been reviewed recently. [2] Australian Chemists have contributed in a very important way to this and other fields of Stereochemistry of Coordination Compounds.

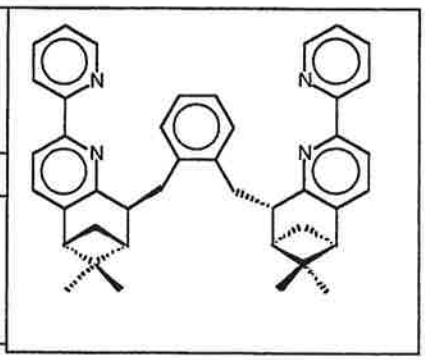
The keys to a class of highly versatile chiral ligands for Coordination Compounds are the two molecules (left side of the scheme):

4,5-pinenebipyridine



5,6-pinenebipyridine





CHIRAGEN Ligand (right)

From these molecules a large family of pluridentate ligands can be derived, as e.g. the CHIRAGEN ligands that are predisposed for coordination in only one absolute configuration to an octahedral metal center.

Configurationally predetermined complexes have now been obtained using such ligands for various coordination geometries, i.e. tetrahedral (T-4), square planar (SP-4), tetragonal pyramidal (TPY-5), trigonal bipyramidal (TBPY-5), and octahedral (OC-6). The metal complexes can be mononuclear or polynuclear. In the latter case, also linear and circular helicates are obtained with predetermined helical chirality.[3][4]

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G.J. BURROWS LECTURE

G.J. BURROWS LECTURE

A.M. Bond
Department of Chemistry, Monash University, Clayton, Victoria 3800

Broadening the Horizons of Inorganic Electrochemistry

Electrochemistry is frequently regarded as a mature 200 year old discipline. For the first century or so of the subject, most studies involved reduction and oxidation of inorganic ions or metals. This initial burst of activity led to a fairly conservative view of what was possible and what was impossible in terms of electrochemical procedures, and so much of the second century advances were limited in scope until the latter part of the century. However, in the last 20 years there have been numerous advances in electrochemistry that now make it possible to study the redox and other aspects of the chemistry of almost every inorganic, organometallic, organic or biologically important compound in solution, solid state or even gaseous phases. For example:

- There are now a vast range of media that can be used other than water (electrolyte), which was traditionally employed for the first 100 years of the discipline.
- A range of exotic electrolytes have been developed and, indeed, studies without added electrolyte are now moderately common.
- Theoretical descriptions of a significant amount of the theory are now available in commercial software packages.
- Studies utilising combinations of spectroscopy, photochemistry and mass spectrometry with electrochemistry are now almost routine. For example, the simultaneous use of Infra-Red, EPR and Electronic Spectroscopy in what are referred to as spectroelectrochemical techniques are now standard procedures used to unravel complex mechanisms.
- Electrodes now range in size from molecular dimension up to meter squared electrodes used for electrorefining of metallic zinc, copper and aluminium.
- Electrochemical techniques employing time scales down to the nanosecond regime are available.

In this lecture, attention will be focussed on the breadth of studies that are now possible which aid new understandings of metal based redox processes. Examples from solution phase and solid state studies will be given, using classical coordination compounds, organometallic compounds and metalloproteins to illustrate the basic principles. Relationships between photoelectrochemistry and electrochemistry and novel uses of the two techniques in combination also will be described. Finally, the limitations that still remain will be summarised and speculation on possible future directions of developments in the subject of inorganic electrochemistry will be considered.

KEYNOTE LECTURES

MOLECULE-BASED MAGNETIC MATERIALS INCORPORATING METAL DICYANAMIDES

K 1

K.S. Murray, S.R. Batten, G.D. Fallon, P. Jensen, B. Moubaraki, D.J. Price, E.H-K. Tan and P. van der Werff.
Department of Chemistry, Monash University, Clayton, Victoria 3800, Australia.
Keith.S.Murray@sci.monash.edu.au

We have recently discovered a new class of homometallic molecule-based magnets based on transition-metal dicyanamide complexes[1] of type α-$(N(CN)_2)_2$. These were found to adopt a single 3D-network rutile-like structure in which the octahedral M(II) ions are connected by three-connecting $N(CN)_2$ ligands. Detailed structural and magnetochemical studies on this isostructural family of compounds made by ourselves[2,3] and two other groups[4,5] revealed a fascinating and diverse array of types of long range magnetic order. The Cu(II) complex is a paramagnet, Co(II) and Ni(II) complexes are ferromagnets and Mn(II) and Fe(II) complexes are spin-canted antiferromagnets (weak ferromagnets), with ordering temperature of les than 20K. Possible reasons for these differences in magnetism will be presented.

A series of 2D-linked compounds of type $M(N(CN)_2)_2(L)$, where M = Mn, Fe, Co, Ni, Cu and L = pyrazine and 4,4'-bipyridine, will also be described, some of which display interpenetrating double-net structures. In the case of L = $2NH_2$-pyrimidine some fascinating square type topologies have been obtained which derive, synthetically, from 1-D $M(N(CN)_2(L)_2$ linear-chain precursors. To date, most of these compounds display weak coupling without long range order, but with most unusual field-dependent data in some cases. Anionic complexes of type $[M(N(CN)_2)_3]^-$ also display sheet-like extended structures and the effects on the magnetism of incorporating various cations and spin centres in to the lattice will be presented.

The present state of development of these structurally varied compounds will be summarised.

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K 2

The Gated Ion Channel Biosensor - a Functioning Nanomachine

R. J. Pace

Ron.pace@anu.edu.au

Co-operative Research Centre for Molecular Engineering & Techonology, 126 Greville Street, Chatswood NSW 2067, Australia
and
Department of Chemistry, The Faculties, The Australian National University, Canberra ACT 0200, Australia

Biosensors combine a biological recognition mechanism with a physical transduction technique. In nature, the transduction mechanism for high sensitivity molecular detection is modulation of cell membrane ionic conductivity, through specific ligand - receptor binding induced switching of ion channels. This affects an inherent signal amplification of 6-8 orders of magnitude, corresponding to the total ion flow arising from the single channel gating event.

Here we describe the first reduction of this principle to a practical sensing device, which is a planar impedance element composed of a macroscopically supported synthetic bilayer membrane incorporating ion channels. The membrane and ionic reservoir are covalently attached to an evaporated gold surface. The channels have specific receptor groups attached (usually antibodies) which permit switching of the channels by analyte binding to the receptors. The device may then be made specific for the detection of a wide range of analytes, including proteins, drugs, hormones, antibodies, DNA, etc., currently in the 10^{-7}-10^{-13} M range. Projected near term sensitivity performance is in the femtomolar range, using flow cell or static well formats

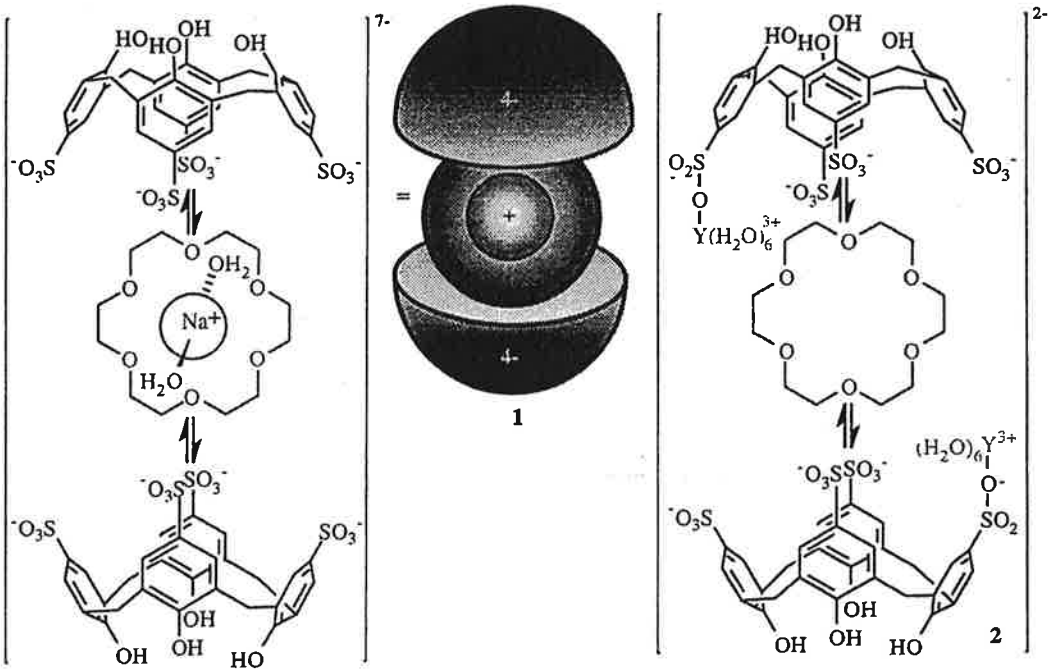
The technology also lends itself readily to microelectronics fabrication and signal transduction. By adjusting the surface density of the receptors / channel components during fabrication, the optimum sensitivity range of the device may be tuned over several orders of magnitude.

Supramolecular Combinatorial Chemistry: Crystallisation of Superanion Capsules ('Russian Dolls') from Aqueous Media

Colin L. Raston

Department of Chemistry, Monash University, Clayton, Melbourne, Victoria 3168 Australia

Recent advances in supramolecular chemistry has allowed the development of a new class of self-assembled water soluble superanion capable of altering its degree of protonation and geometrical configuration to accommodate the charge and size of a broad range of polynuclear aqua cations.[1] This globular like superanion or ionic capsule consists of two sulfonated calix[4]arene molecules which encapsulate a central sodium cation bound by a crown ether and two *trans*-water molecules, **1**. A range of cohesive supramolecular interactions are important in the solid state including hydrogen bonding, electrostatic, π-stacking, and van der Waals. The ability of the superanion to interact with a range of polynuclear aqua cations with different charge, size and shape in a common structural moiety has been demonstrated by its cocrystallisation with a number of novel polynuclear Cr(III) hydrolysis products: $[Cr_2(OH)_2(H_2O)_8]^{4+}$, $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$, and $[Cr_4(OH)_6(H_2O)_{12}]^{6+}$, in some cases allowing structural authentication for the first time.[1] This technology has been applied to selectively isolate and structurally characterise a labile main group metal hydrolytic Keggin ion, $[Al_{13}O_4(OH)_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. Related superanions are formed in the presence of lanthanide ions, over very narrow pH range, e.g. **2**, [2] and also with tetraprotonated cyclam in place of 18-crown-6.[3]



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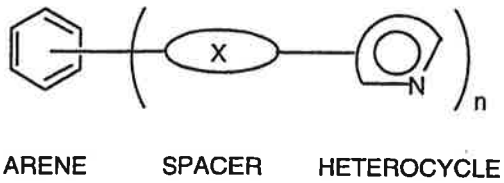
NEW METALLOSUPRAMOLECULAR ARCHITECTURES

Peter J. Steel

Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

Email: p.steel@chem.canterbury.ac.nz

We have synthesised a large range of ligands, represented by the general structure **1**, that contain a central arene core to which varying numbers of heterocyclic groups are attached, via spacer groups (X). By changing the various parameters within this generalised structure, it is possible to encode information into these ligands, such that upon reaction with appropriate metal ions they undergo controlled self-assembly to produce metallosupramolecular species with diverse topologies. Examples will be given of the syntheses of various one-, two- and three-dimensional structures, including molecular boxes, ladders, cages, grids and helicates. A specific example is the first quadruply-stranded metal helicate **2**.



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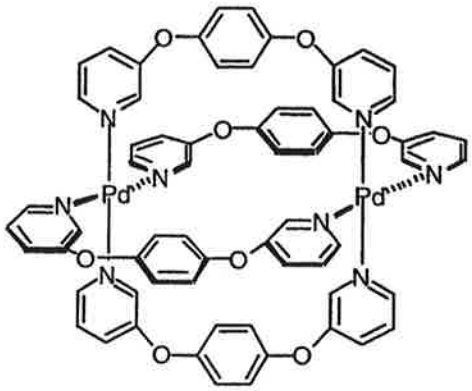


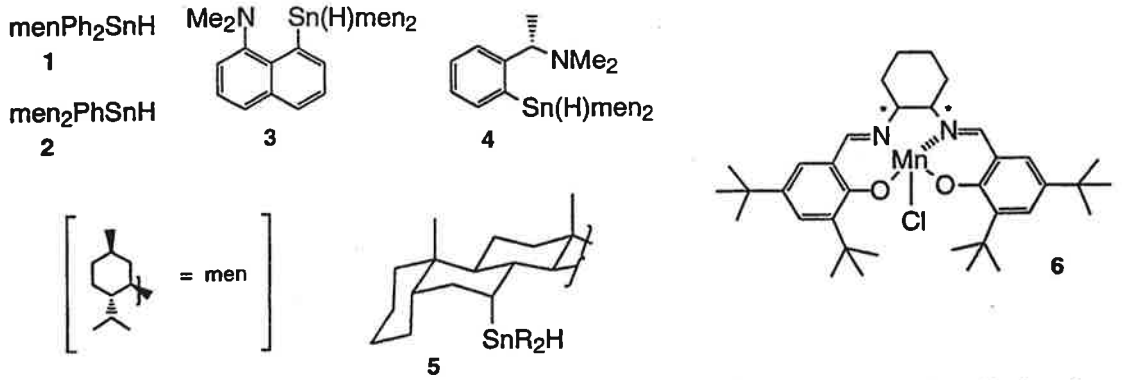
(2)

CHIRALITY TRANSFER - THE QUEST FOR SINGLE-ENANTIOMER OUTCOMES IN FREE-RADICAL CHEMISTRY

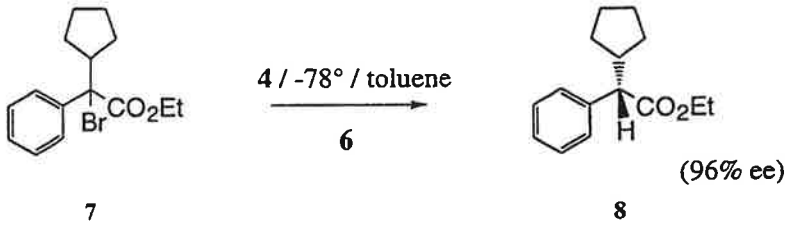
Carl H Schiesser

School of Chemistry, The University of Melbourne, Parkville, Victoria, Australia, 3052
(c.schiesser@chemistry.unimelb.edu.au)

Despite there being numerous reports of free-radical reactions proceeding with diastereocontrol,[1,2] there are relatively few examples of free-radical reactions which proceed with genuine enantiocontrol.[2] The majority of examples that demonstrate enantioselective outcomes involve the use of chiral auxiliaries and, as a result, are further examples of diastereoselectivity in free-radical chemistry.[1,2] Of the remaining few reports, the introduction of asymmetry in the substrate through the use of chiral Lewis acid mediation,[3,4] and in the reagent through the use of chiral ligands on the tin atom in suitably constructed stannanes[5-8] have been the methods of choice for achieving enantioselectivity in radical chemistry.



Our approach to the development of synthetically useful chiral stannanes primarily involves the judicious choice of ligand from the multitude of compounds available in the natural chiral pool. This presentation will discuss the synergistic effect of Lewis acid and stannane on the stereochemical outcome of reductions involving chiral stannanes. Significant improvements in enantioselectivity in reductions involving simple chiral non-racemic stannanes (**1** – **5**) are achieved by the addition of Lewis acids. For example treatment of racemic ethyl 2-bromo-2-cyclopentyl-2-phenylacetate (**7**) with **4** at -78° in toluene in the presence of and (*S,S*)-(-)-N,N'-bis(3,5-di-*tert*-butylsalycidene)-1,2-cyclohexanediaminomanganese(III) chloride (**6**) affords (*S*)-ethyl 2-cyclopentyl-2-phenylacetate (**8**) in good yield and in 96% ee.[9]



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K 6

Acid-base Behavior with Trinuclear Carbeniato Complexes of Gold(I). Intercalation by Cations and a Molecular Acid.

Alfredo Burini‡, John. P. Fackler, Jr., R. Galassi, B. R. Pietroni, and R. J. Staples
Texas A&M University, College Station, TX. 77843-3012:e-mail: Fackler@mail.chem.tamu.edu,
‡Dipartimento Di Scienze Chimiche, Camerino, Italy.

Trinuclear Au(I) clusters with pyrazolate and carbeniato ligands have continued to produce interesting chemistry since the first reports by Vaughan and by Bonati and co-workers. Surprisingly different oxidative-addition patterns have emerged for the carbeniato and pryazolato species. An exceptional solvoluminescence has been observed by Balch with a carbeniato complex and cation π interactions have been reported by us with Ag(I) bonded to two trinuclear benzimidazolato Au(I) complexes. While Tl(I) has been known to produce short Tl-Au interactions for some time, the fact that Tl(I) can occupy essentially the same position as Ag(I) was unexpected, with coordination to the six Au(I) atoms upon intercalation into the trinuclear benzimidazolato Au(I) complex. Furthermore, it has been found that the molecular acid $[Hg_3(C_6F_4)_3]$ also intercalates into the planar cluster to produce a spectacular linear chain of these trinuclear acid-base entities, $\{[Au(\mu\text{-}N,C)\text{-}(ethoxy)(N\text{-}p\text{-}tolylimmino)methyl]_3\}_2$ $[Hg_3(C_6F_4)_3]$. Each of these compounds display intermolecular Au-Au interactions and photoluminescence.

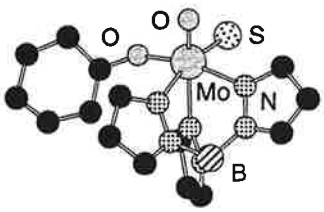
Toward the First Model for the Molybdenum Hydroxylases

Charles G. Young,[a] Paul D. Smith,[a] Damian A. Slizys[a] and Graham N. George[b]

[a] School of Chemistry, University of Melbourne, Victoria 3010. [b] Stanford Synchrotron Radiation Laboratory, SLAC, Menlo Park, CA 94309, U.S.A.

A broad synthetic model for the molybdenum hydroxylases, which catalyse the activation and oxidation of substrate C-H bonds at biologically unique oxo–thio–Mo(VI) active sites, is yet to emerge. Few oxo–thio–Mo(VI) complexes are known and none of these possess Mo(V) and Mo(IV) counterparts representing the enzymes' oxo–thio– and oxo(hydrosulfido)–Mo(V) states or participate in clean biomimetic chemistry.[1]

A major aim of our research has been the synthesis of an oxo–thio–Mo(VI) complex which could serve as the cornerstone for a broad model of enzyme active site structure, spectroscopy and reactivity. Toward this end we have recently focused on bulky hydrotris(3–isopropylpyrazol–1–yl)borate (L^{Pr}) complexes having the capacity, by virtue of carefully selected co–ligands, to resist internal redox[2] or other undesirable side–reactions.[3] Here, we describe the synthesis and characterisation of the monomeric oxo–thio–Mo(VI) complex, $L^{Pr}MoOS(OPh)$ (**1**, below – Pr groups not shown), its facile equilibrium with a μ–disulfido–Mo(V) dimer, $[L^{Pr}MoOS(OPh)]_2$ (**2**), the generation and isolation of the corresponding oxo–thio– and oxo(hydrosulfido)–Mo(V) complexes, and some biomimetic chemistry of these complexes. The enzyme model described is the first to feature inter–convertible, biologically relevant, $[Mo^{VI}OS]^{2+}$, $[Mo^{V}OS]^{+}$ and $[Mo^{V}O(SH)]^{2+}$ centres having common co–ligands and structural, spectroscopic and chemical properties relevant to the enzyme systems.



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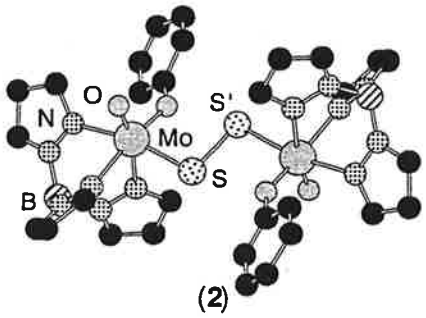

(2)

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REDOX ACTIVATION OF THE IRON MOLYBDENUM COFACTOR OF NITROGENASE

Kylie Vincent,[a] Christopher J. Pickett[b] and Stephen P. Best[a]

[a] School of Chemistry, University of Melbourne, Parkville, 3052 Victoria, Australia
[b] Nitrogen Fixation Laboratory, John Innes Centre, Norwich Research Park, Norwich NR4 7UH, UK.

Email: s.best@chemistry.unimelb.edu.au

In contrast to the high-temperature, high-pressure Haber-Bosch process, biological nitrogen fixation is achieved under ambient conditions by the primordial bacteria on which all higher life-forms rely. Attempts to elucidate or emulate the enzymatic process have been at the forefront of biochemical and chemical research for more than four decades. This paper focusses on the intact nitrogenase cofactor (FeMoco), an isolable iron-molybdenum-sulfur cluster responsible for dinitrogen binding and activation (Fig. 1). We report studies of the redox state dependence of the binding of substrates (CO and Bu^{t}NC) to FeMoco.

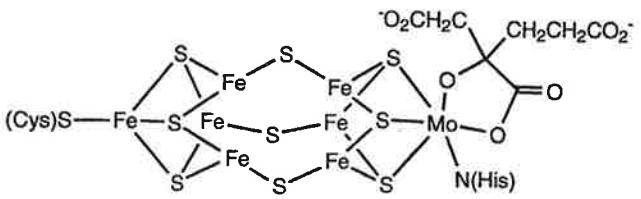


Fig. 1 X-ray structure of FeMoco.

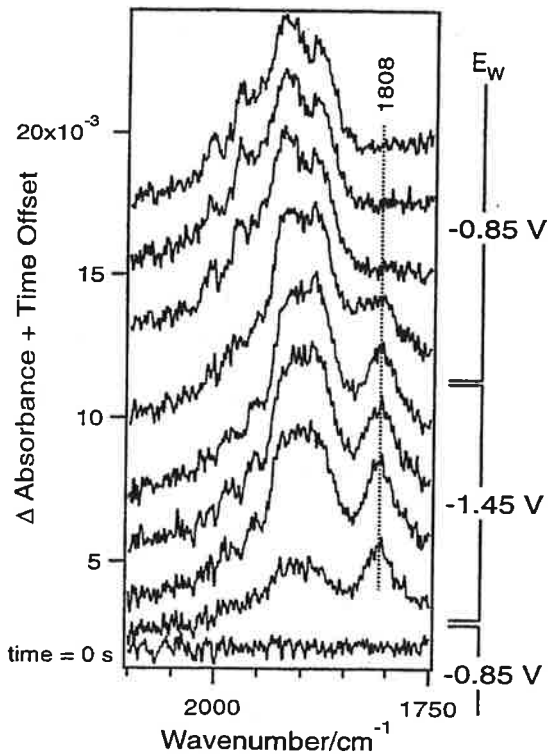


Fig. 2. IR-SEC spectra of FeMoco/CO at intermediate [CO]. Time between spectra = 12.4 s.

The IR spectra in the ν(CO) region shown in Fig. 2 were recorded from an NMF solution of FeMoco (*ca.* 2 mM) at intermediate dissolved CO concentration. Spectra were computed from 10 co-added scans of the FTIR. The growth of bands in this region is associated with the formation of FeMoco:CO complexes. The redox dependence of the spectral changes indicate that reduction of FeMoco beyond the semi-reduced state is necessary in order for there to be significant FeMoco:CO interaction. The character of the complexes formed in these experiments depends both on the identity of the substrate and other potential ligands present in the system. These experiments provide an immediate link to the EPR and IR measurements conducted on nitrogenase during turnover in the presence of CO.

S.K. Ibrahim, K. Vincent *et. al.*, J. Chem. Soc. Chem. Commun. 1999, 1019.

HELICAL COMPLEXES - MORE THAN PRETTY STRUCTURES.

K 9

L.J. Charbonnière, C. Provent, S. Telfer, and A.F. Williams*,

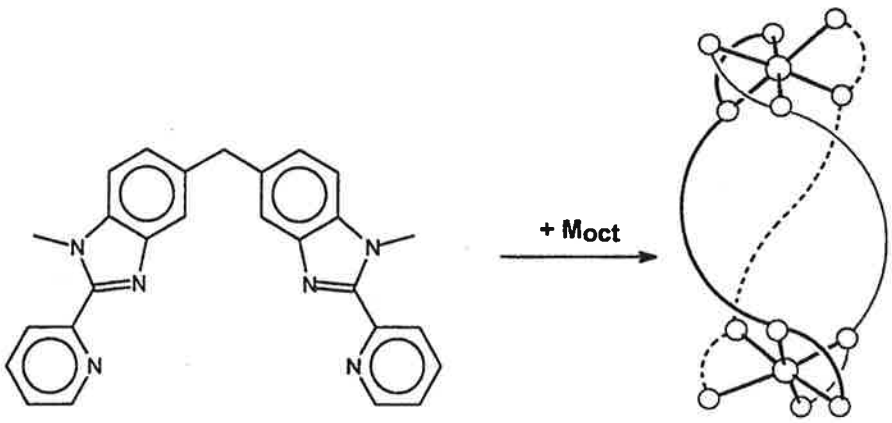
Department of Inorganic Chemistry, University of Geneva, 30 quai Ernest Ansermet, CH 1211 Geneva 4, Switzerland. e-mail: Alan. Williams@chiam.unige.ch

*On leave at Research School of Chemistry, Australian National University, Canberra, ACT 0200 Australia.

Helical metal complexes, or helicates, have attracted much attention over the past ten years. The ease with which symmetric, high molecular weight complexes may be prepared in virtually quantitative yield is remarkable, and the helicates have established themselves as classical examples of self-assembly reactions in supramolecular chemistry. Much less attention has been paid to the properties of these complexes.

The first half of this lecture will give a brief review of the principles of construction of the helicates, together with an analysis of the factors which control the structure, including effects which are frequently overlooked such as solvent, concentration and π-stacking interactions.

The second half will be concerned with the properties of the helicates, and in particular the often remarkable differences between dinuclear helicates and analogous mononuclear complexes. Thus helicates show higher thermodynamic stability and greater kinetic inertness than mononuclear systems. In dinuclear complexes the interaction between metal centres has been studied for mixed valence complexes, spin crossover for iron(II) and cooperativity in metal exchange.



STRUCTURE DETERMINATIONS OF SMALL MOLECULE BINDING TO HEME PROTEINS USING EXAFS

K 10

Robert S. Armstrong,[a] Ming-Chu Cheng,[a] Paul J. Ellis,[a] Peter A. Lay,[a] William Montfort,[b] Anne M. Rich,[a] Roland Stocker,[c] Linda Tennant,[d] Sushila Thomas,[a] F. Ann Walker,[b] Peter E. Wright[d]

[a]School of Chemistry, University of Sydney, NSW, 2006
[b]Department of Biochemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.
[c] Heart Research Institute, 145-147 Missenden Road, Camperdown, NSW, 2050
[d] Department of Molecular Biology, Research Institute of Scripps Clinic, 10666 Nth Torrey Pines Rd, La Jolla, CA, 10550, U.S.A.

lay_p@chem.usyd.edu.au

As part of a continuing program, XAFS data have been obtained from frozen aqueous solutions (10 K) of Fe(II) and Fe(III) cytochrome *c* (cyt *c*), horse heart myoglobin (Mb), soybean leghemoglobin *a* (Lb *a*), nitrophorin (NP) and indoleamine-2,3-dioxygenase (IDO) and their small molecule adducts with NO, O_2 and CO. The binding of small molecules and in particular NO to these molecules has aroused considerable interest, as the diverse physiological roles of NO have become apparent. The binding of NO to Hb and Mb are believed to be important in the transport of NO and in the health of the heart and vein walls. NPs are a class of proteins that are used by blood sucking insects (*Rhodnius prolixus*) to transport NO to the blood of the host animal where it is used as a vasodilator. Lb is a plant heme protein than is used to control O_2 to nitrogen-fixing bacteria, but also appears to bind NO as a control mechanism to regulate O_2 levels. Finally, IDO is believed to bind NO as a control mechanism for its normal role in the immune system.

The structures of the Fe sites have been refined using both single-scattering (SS) and multiple-scattering (MS) analyses. The XAFS MS analyses yield more precise Fe-ligand bond lengths (estimated error 0.02 – 0.03 Å) than those determined previously from X-ray crystal data for cyt *c* (estimated errors ≥ 0.1 Å).[1,2] For both forms of cyt *c*, the Fe–N(pyrrole) distances are 1.98-1.99 Å and the Fe–N(imidazole) distances 1.98-2.00 Å. The Fe–S(methionine) distance of Fe(II) cyt *c* (2.29 Å) is shorter than for Fe(III) cyt *c* (2.33 Å), although the values are not significantly different. The small changes in bond lengths are consistent with the fast electron transfer of cyt *c*.[2]

In all of the proteins, the Fe(III)–NO adducts are close to linear whereas the Fe(II)–NO adducts are bent (~140-150°).[3,4] However, these species may be five- or six-coordinate depending on the physiological role. Finally, the large differences in XRD-determined Fe–O–O bond angles among O_2 adducts of Hb, Mb and Lb that are discussed in biochemical textbooks, are not apparent in the XAFS results. These putative differences may be an artifact of crystal packing forces that result from the diffusion of small molecules into preformed crystals used for XRD analysis.

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SUPER ANIONS AND SUPERACIDS

Christopher A. Reed, Kee-Chan Kim, Robert D. Bolskar, and Daniel Stasko

Department of Chemistry, UC Riverside, Riverside, CA 92521-0403

Email: chris.reed@ucr.edu

Inert yet functionalizable, icosahedral carborane anions based on $CB_{11}H_{12}^-$ are finding applications across organic and inorganic chemistry.[1] The hexahalo derivatives $CB_{11}H_6X_6^-$ are amongst the most inert, least coordinating anions presently known, allowing the exploration of new extremes in reactive cation chemistry.

They can support the fierce Lewis acidity of the silylium ion in species such as $R_3Si(CB_{11}H_6Cl_6)$.

They can support high Bronsted acidity, even superacidity, in salts of protonated arenes (so-called Wheland intermediates in electrophilic aromatic substitution). $[H(benzene)]^+[CB_{11}H_6Cl_6]^-$ is a stable, weighable, crystalline salt at room temperature. Evidence will be presented for the existence of the unsolvated conjugate acid, $H(CB_{11}H_6Cl_6)$. It is remarkable that the B-H and B-Cl bonds are stable to superacid $[H^+]$ strength.

$CB_{11}H_6X_6^-$ anions can also support very strong one-electron oxidants such that, for example, a salt of C_{60}^+ can be isolated.

There is commercial interest in these reagents because of their potential use as cocatalysts in cationic alkene polymerisation.

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ORAL PRESENTATIONS

Near-Infrared to Visible Upconversion in Rare-Earth Doped Halide Host Materials

S.R. Lüthi
Department of Chemistry, University of Queensland, St. Lucia, Brisbane QLD - 4072, Australia, eMail: luethi@chemistry.uq.edu.au

H.U. Güdel
Department of Chemistry and Biochemistry, University of Berne, Freiestrasse 3, CH-3012 Bern, Switzerland

Upon excitation in the near-infrared, a series of trivalent rare-earth ions emit light in the visible and near-ultraviolet spectral range. In the last years, there has been renewed interest in upconversion processes, first found in 1966 by Auzel [1], due to the availability of diode lasers as highly efficient pump sources in the near-infrared. Most of the work on energy-upconversion has been done on rare-earth doped oxide and fluoride hosts. Our approach is to use chlorides, bromides, and iodides. These heavier halides have lower phonon energies, which leads to a significant reduction of multiphonon relaxation rates. Excited states with negligible population in an oxide or fluoride compound can thus become important in a chloride, bromide or iodide, for both radiative and nonradiative processes such as luminescence and upconversion, respectively [2]. By simple substitution of the halide ions in the host material, we can tune the energy-level structure and spectrosopic properties. The principle of chemical variation turns out to be very successful in this research [3]. We are developing techniques to differentiate between the different upconversion mechanisms and are exploring theoretical models to more thoroughly understand the experimental situations [2-5].

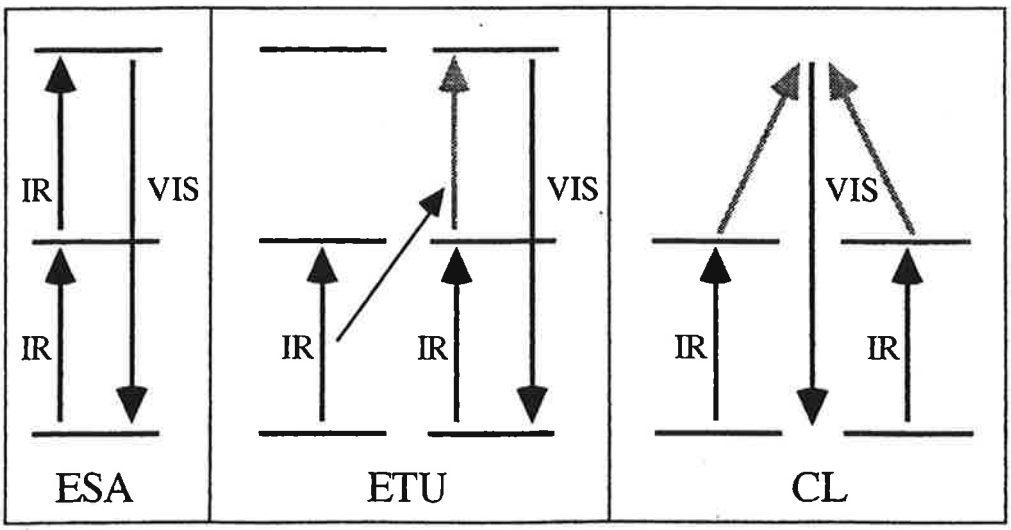

Figure: Schematic representation of three important energy-upconversion processes: Excited state absorption (ESA) on a single ion, energy transfer ucponversion (ETU) and cooperative luminescence (CL), both requiring the interaction of two ions.

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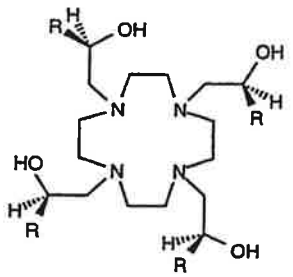
OP 2

METAL ION ACTIVATED SUPRAMOLECULAR RECEPTORS

Christopher B. Smith*, Kia S. Wallwork*, Stephen F. Lincoln‡, Max R. Taylor* and Kevin P. Wainwright*

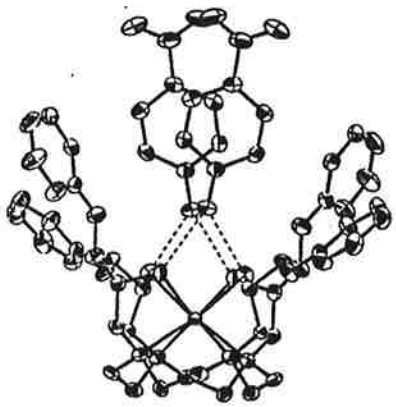
*School of Chemistry, The Flinders University of South Australia, GPO Box 2100, Adelaide, South Australia 5001 and ‡Department of Chemistry, University of Adelaide, Adelaide 5005
E-mail: Kevin.Wainwright@flinders.edu.au

Pendant donor macrocycles derived from cyclen (1,4,7,10-tetraazacyclododecane) invariably coordinate to a metal ion in such a way that all four pendant arms project in the same direction.[1] If, in addition to carrying a pendant donor group, these arms also have a phenyl or naphthyl group attached to them the possibility arises of using the coordination of the ligand to a metal ion as a way of assembling a molecular receptor with a substantial hydrophobic cavity that arises from the juxtaposition of the four phenyl or naphthyl groups. Upon removal of the metal ion the ligand can lose this conformation and consequently release any guest molecule that has been captured by the complex (the host). We have now prepared a range of these ligands, **1 - 7**, and have begun to study their coordination and host-guest chemistry.



1 R = Ph (*R*-thpec12)
2 R = $PhCH_2$-
3 R = $PhOCH_2$-
4 R = 1-naphthylOCH_2-
5 R = 2-naphthylOCH_2-
6 R = 4-phenylphenylOCH_2-
7 R = 4-$PhCH_2OPhOCH_2$-

As an illustration of this, complexation of **3** with cadmium(II) or lead(II) leads to eight coordinate complexes, which, as their perchlorate salts, have the desired cavity devoid of any guest molecule. This has been verified by X-ray crystallography and is known to persist in solution from NMR and conductivity data.[2] Upon reaction with the sodium salts of a variety of aromatic oxoanions, sodium perchlorate is eliminated and inclusion complexes containing the aromatic oxoanion can be formed. As an example, the inclusion complex derived from the Cd(II) complex of **3** and two *p*-nitrophenolate anions is shown in the adjacent ORTEP diagram, and is known, from conductivity studies, to exist also in solution. In the solid state each *p*-nitrophenolate is retained by two hydrogen bonds, as shown, and there is offset centroid, face to face alignment of the *p*-nitrophenolate aromatic rings with an interplane separation of *ca.* 3.3 Å.



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The Supramolecular Chemistry of the Heavily Phenylated Ligands, $Ph_2P(CH_2)_nPPh_2$ (n = 1 to 4)

Gareth R. Lewis and Ian Dance
School of Chemistry, University of New South Wales, Sydney 2052, Australia
gareth.lewis@unsw.edu.au

The supramolecular interactions between phenyl rings is well documented, in particular the formation of energetically attractive motifs between compounds containing multiple phenyl rings, such as $[PPh_3R]^+$ (R = Me or Ph], $[M(PPh_3)_n]$ and $[Ph_3PNPPh_3]$.[1] Analysis of the CSD (May 1999 release, version 5.17a) yields over 2200 crystal structures containing one or more of the ligands $Ph_2P(CH_2)_nPPh_2$, denoted dppx, where x is the length of the aliphatic chain. Investigation of the structures with short intermolecular P•••P separations shows the formation of mutually attractive supramolecular motifs between neighbouring dppx ligands (Figure). Here we present the nature of the different interactions between the dppx ligands, the magnitude of the attraction between ligands and the proportion of compounds that adopt these supramolecular motifs

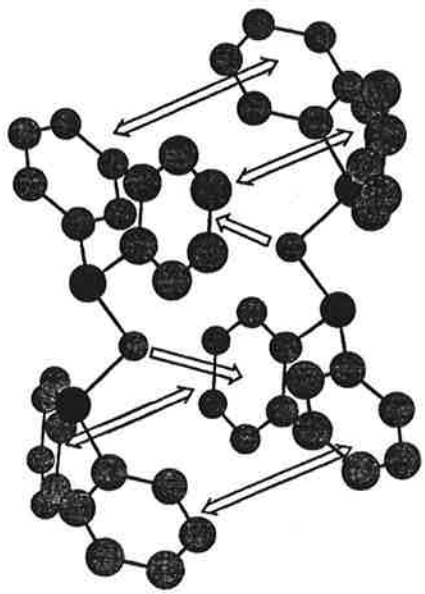

Figure. Pairwise interaction between two dppm ligands. Single arrows indicate a C-H•••π interaction between a CH_2 group and a phenyl ring. Double arrows indicate a non-parallel offset face-to-face arrangement of phenyl rings.

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CRYSTAL ENGINEERING HOST-GUEST SYSTEMS: ASSEMBLY OF COORDINATE AND H-BONDED ARRAYS WITH CTV AND INORGANIC CAGE MOLECULES.

Michaele J. Hardie , Colin L. Raston and Bradley Wells

Department of Chemistry, Monash University, Clayton, Victoria 3800, Australia.

The bowl-shaped container molecule cyclotriveratrylene (= CTV) shows a rich host-guest chemistry in solution and the solid state and can bind large spherical inorganic cage molecules such as fullerene-C_{60} and 1,2-dicarbadodecaborane(12) ($C_2H_{12}B_{10}$ = *o*-carborane).[1] Such complexes show a wide range of supramolecular interactions including complementarity of curvature, hydrogen bonding and π-π interactions. It has recently been shown that CTV can be incorporated into infinite solid state arrays (or crystal engineered systems) through bifurcated hydrogen bonding interactions between the dimethoxy moieties of the CTV and acidic protons such as those found on *o*-carborane. This alters CTV's properties as a host molecule allowing, for instance, the complexation of higher fullerenes such as C_{70} by CTV for the first time.[2]

We report herein the X-ray crystal structures of a number of such hydrogen bonded networks involving CTV, carboranes and higher fullerenes. The four component supramolecular system (C_{70})(*o*-carborane)(CTV)(1,2-dichlorobenzene) is chiral, assembling into infinite helical arrays. Initial results indicate that a fullerene-C_{76} complex is isostructural which may provide a methodology for the chiral resolution of fullerene-C_{76}.

Another approach is to use CTV as a ligand for main group metals or lanthanides, illustrated by the crystalline complex $[Na(OH)(H_2O)_2(CTV)_2](o\text{-carborane})_2(DMF)_2$ where each Na^+ is coordinated by two chelating CTVs and two hydroxide/water molecules (shown right). This assembly hydrogen bonds to water to create an extended 2D network, and DMF and *o*-carborane acts as guest molecules within the lattice.

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OP 5

XAFS Studies of Ruthenium and Osmium Dinitrogen Ammine Complexes

Robert S. Armstrong,[a] Fei Chen,[a] Garry J. Foran,[b] Dominic Hodson,[a] Peter A. Lay[a]

[a] School of Chemistry, University of Sydney, NSW, 2006

[b] Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW, 2234

R.Armstrong@chem.usyd.edu.au

Structural characterization of dinitrogen complexes, $[M(NH_3)_5(N_2)]^{2+}$ (M = Ru, Os), *cis*-$[Os(NH_3)_4(N_2)_2]^{2+}$, $[(NH_3)_5MNNM'(NH_3)_5]^{n+}$ (M = Ru, Os; M′ = Ru, Os; n = 4, 5, 6), *cis*-$[(NH_3)_4ClOsNNOs(NH_3)_5]^{n+}$ and *cis,cis*-$[(NH_3)_4ClOsNNOsCl(NH_3)_4]^{n+}$ have been studied by X-ray absorption fine structure (XAFS). Both the XAS obtained from Ru (K edge) and Os (L3 edge) have been fitted. It is not possible to study all of these structures by X-ray diffraction because of disorder in Ru/Os complexes and the instability of some oxidation states, which precludes the growing of crystals. The XAFS results have enabled systematic studies into the effects of π backbonding on the N–N bond length as a function of the metal ion and the oxidation state. Such studies are important with respect to understanding N_2 activation in relation to nitrogenase.

OP 6

Using Copper Atoms to Bind Alkanephosphonates to Gold Surfaces

Murray Baker,[1] G. Kane Jennings,[2] and Paul E. Laibinis[3]

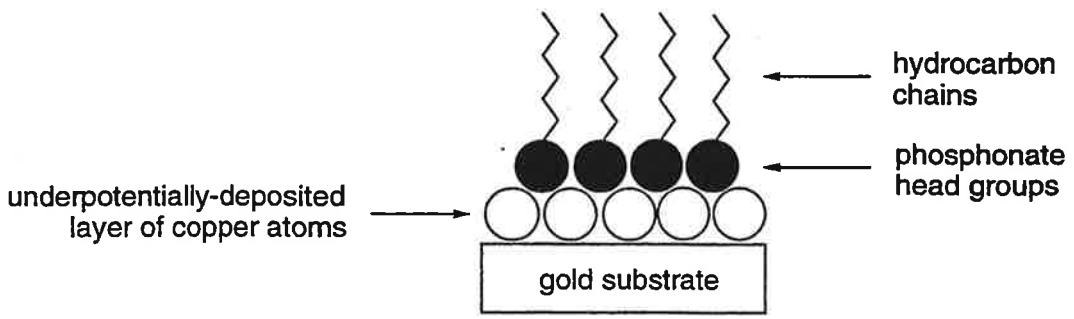
[1] Department of Chemistry, The University of Western Australia, Nedlands, WA 6907. (mvb@chem.uwa.edu.au)

[2] Department of Chemical Engineering, Vanderbilt University, Nashville, TN 37235 USA.

[3] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA 02139 USA.

Gold is often used in the construction of electrochemical sensors and other devices because it is highly conductive, it resists oxidation by air, and it can be easily evaporated to produce platforms such as thin films, interdigitated electrodes, and metal interconnects. For applications which require surface-modified electrodes, gold can be functionalised by the formation of organic monolayers on its surface. The organic compounds that can adsorb to gold to form these monolayers are, however, limited to those that contain a "soft" coordinating atom, such sulfur (in RSH and RSSR) or phosphorus (in PR_3). Organic functionalities such as alkanephosphonates (RPO_3^{2-}) and carboxylic acids, which are dominated by "hard" atoms and have a strong affinity for oxide surfaces such as ZrO_2, TiO_2, and Al_2O_3, show little or no affinity for gold. Alkanephosphonates interact strongly with many transition metal ions, including Cu, to form layered crystalline materials, and have attracted interest as agents for the formation of Langmuir-Blodgett films. However, the phosphonate group is a "hard" group and alkanephosphonates do not interact strongly with gold to form stable monolayers on this substrate.

Underpotential deposition is an experimentally simple electrochemical technique that can be used to deposit a sub-monolayer coverage of metal atoms onto a bulk sample of a different metal. In this presentation, we show that the affinity of alkanephosphonates for the gold surface can be readily modified by the presence of an underpotentially-deposited layer of copper. A single atomic layer of copper is sufficient to allow formation of robust alkanephosphonate monolayers on gold and to retain the ability of the gold substrate to function as an electrode. Simple experiments that can be used to probe the influence of the underpotentially-deposited layer on the stability of the gold/monolayer interaction will also be discussed.



OP 7

SPECIFIC ANION INTERACTIONS WITH (POLYPYRIDYL)RUTHENIUM COMPLEXES

Brett D. Yeomans,[a] Laurence S. Kelso,[a] Nicholas C. Fletcher,[a]
Peter C. Junk,[a] Peter A. Tregloan[b] and F. Richard Keene[a]

[a] *School of Biomedical and Molecular Sciences, James Cook University, Townsville Qld 4811, Australia.*

[b] *School of Chemistry, University of Melbourne, Parkville Vic 3052, Australia.*

{E-Mail: Richard.Keene@jcu.edu.au}

We have recently developed a cation-exchange chromatographic technique for the separation of stereoisomers of mono- and oligonuclear complexes, generally involving ruthenium and osmium metal centres with polypyridyl ligands.[1-3] Specific examples of its application include the chiral resolution of a wide range of mononuclear tris(bidentate)ruthenium(II) complexes,[4] the separation of geometric isomers of mononuclear complexes containing unsymmetrically-substituted bidentate ligands,[5] the separation of diastereoisomeric and enantiomeric forms of a range of di- and tri-nuclear species,[3] and the resolution of a di-iron double helix involving a hexadentate polypyridyl ligand.[6]

Mechanistic investigations of the chromatographic separation have identified the involvement of specific interactions between eluent anions and the substrate complex.[1,2] These interactions have both hydrophobic and π-stacking components, and vary between different complexes and between stereoisomeric forms of the same complex, thereby promoting the separations.

The paper will summarise a multi-faceted approach to elucidate the nature of these important interactions.

1. Structural studies of the interactions of anions with polypyridylruthenium complexes.[4]
2. NMR titration studies of the dependence of the chemical shifts of ligand and anion protons on complex:anion ratios.[2]
3. Anion dependencies of electrochemical characteristics.[7]
4. High-pressure electrochemical studies.[7]
5. Anion dependencies of luminescence properties.[2]

The paper will discuss our present understanding of the anion-complex interactions, whose implications extend beyond the chromatographic separations, to (for example) the nature of interactions of metal complexes with biological molecules such as DNA.

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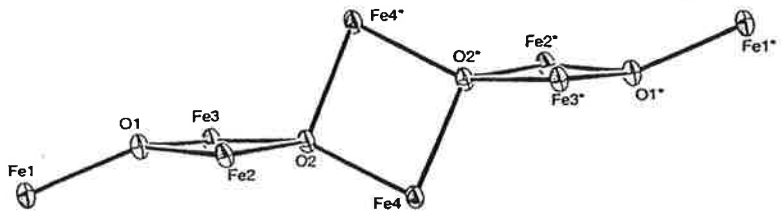
Reactions of "Basic" Fe(III) Carboxylates with Metal Alkoxides and Alcohols.

Paul Ammala, John D. Cashion†, Christopher M. Kepert, Boujemaa Moubaraki, Keith S. Murray, Leone Spiccia, Bruce O. West

Department of Chemistry, Monash University, Clayton, Vic. 3168.
†Department of Physics, Monash University, Clayton, Vic. 3168.

Interest in iron-oxo clusters in general, stems from the ability of these compounds to model the bio-mineralisation of iron[1] and to generate magnetic materials with high-spin ground states[2]. "Basic" iron(III) carboxylates have been widely used as precursors in the synthesis of such iron-oxo clusters including Fe_{10}[3] and Fe_{11}[4] compounds, although the condensation mechanism by which such species are generated remains unclear.

Our interest in mixed-metal complexes as potential precursors to the preparation of mixed metal oxides by sol-gel processing, led us to explore the reactions of "basic" iron benzoate with titanium(IV) alkoxides in alcohol. Initial investigations into these reactions indicated that an exchange of alkoxide and carboxylate groups was occurring. Such reactions were thought to result from group exchange between the Fe and Ti starting materials, however, since the decanuclear "ferric wheel" compounds $[Fe(OR)_2(O_2CR')]_{10}$ had resulted from reactions of "basic" iron carboxylates in MeOH, it was postulated that an alkoxy-carboxylate complex might be formed by reaction of $[Fe_3(\mu_3\text{-}O)(O_2CPh)_6(H_2O)_3](O_2CPh)$ with alcohol. Direct reactions of "basic" iron(III) benzoate with alcohols allowed the isolation and structural characterisation of a novel octanuclear iron(III) oxo complex containing an $\{Fe_8(\mu_3\text{-}O)_2(\mu_4\text{-}O)_2\}^{16+}$ core supported by alkoxide and carboxylate bridging groups. $Fe_8(\mu_3\text{-}O)_2(\mu_4\text{-}O)_2(\mu_2\text{-}OCH_2Bu^t)_2(\mu_2\text{-}O_2CPh)_{12}(O_2CPh)_2(Bu^tCH_2OH)_2$ **[1]** exhibits a chain-like Fe_8O_4 spine that is unique amongst the family of iron-oxo clusters and shows a lower degree of condensation than previously reported Fe_8 structures. It is the first iron-oxo core to be isolated which is comprised of two Fe_4O_2 "butterflies", with links occurring via the two μ_4-oxo groups.



"Double-butterfly" Core Structure of **1**.

Further reactions of "basic" iron(III) carboxylates with metal alkoxides have lead to a series of novel homo- and hetero-metallic iron derivatives. The structures and properties of these materials will be presented.

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Molecular Engineering at the Active Site of Rubredoxin

OP 9

M. Cross, Z. Xiao, M. Maher,† M. Guss† and A.G. Wedd

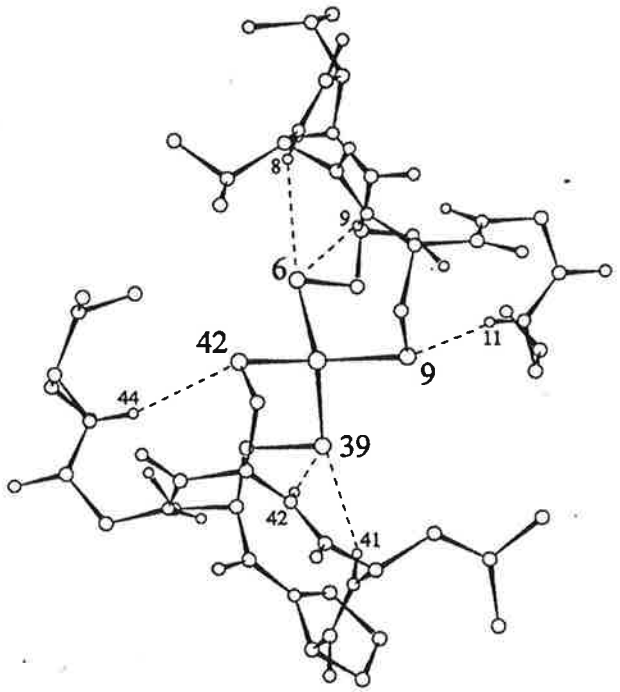
School of Chemistry, University of Melbourne, Parkville, Vic. 3052
†School of Biochemistry, University of Sydney, Sydney, NSW 2006
(t.wedd@chemistry.unimelb.edu.au)

The engineering of a known protein active site to produce new reactivities is now possible via genetic techniques. The aim here is to induce new properties in rubredoxin, a simple iron-sulfur redox protein, by metal and ligand substitution and by mutations which vary access to the active site.

Rubredoxin features a single $Fe(S\text{-}cys)_4$ centre (Figure: D_{2d} local symmetry). This poster will discuss:-

(i) The Pr^i sidechains of V8 and V44 protect the active site (Figure). Their systematic substitution by alkyl groups of differing volume allows assessment of the influence of solvent access upon redox potential.[1] The substitution of V8 by A effectively converts the present protein into that from another bacterium (*D gigas*), as predicted theoretically.

(ii) The thiolate sidechains of C9 and C42 on the molecular surface provide two of the ligands to the iron atom (Figure). Elimination of C42 allows assembly of a Fe_2S_2 cluster in a site designed for a simple Fe centre! The nature of the new sites imposed by mutation of these cystein ligands will be outlined.



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OP 10

REACTIVITY OF CIS-BIS(ALKENE)-BIS(ACETYLACETONATO)RUTHENIUM(II) COMPLEXES WITH GROUP 15 DONOR LIGANDS

Martin A. Bennett†, Matthew J. Byrnes†, Guandolina Chung†, Alison Edwards†, Graham A. Heath†, Brian E. Mann*, Horst Neumann† and Anthony C. Willis†

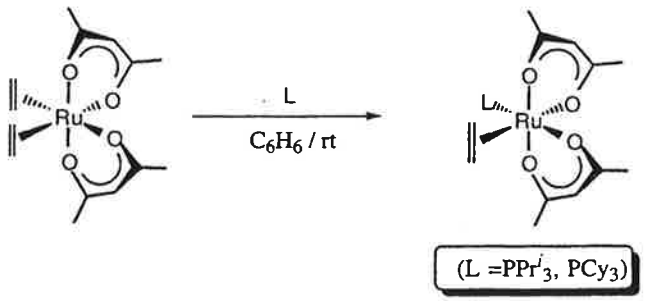
† Research School of Chemistry, Australian National University, Canberra 0200

byrnes@rscsun.anu.edu.au

* Department of Chemistry, the University of Sheffield, S3 7HF, England

Reduction of [Ru(acac)$_3$] with Zn/Hg or activated Zn dust in aqueous THF in the presence of excess cyclooctene[1] or ethylene[2] gives the labile bis(alkene) complexes *cis*-[Ru(acac)$_2$(η^2-alkene)$_2$] (alkene = C_8H_{14} (**1**), C_2H_4 (**2**)]. Both alkenes are readily displaced at room temperature by ligands to give the *trans*-isomers of [Ru(acac)$_2$L$_2$] (L = NMe_3, PPh_3, $PPhMe_2$, PMe_3, $P(OMe)_3$, $AsPh_3$, pyridine and Bu^tNC),[1] which isomerise, on heating, to their *cis*-counterparts (except for NMe_3). Monitoring of the reaction between **1** or **2** and PR_3 (1 equiv) in THF by $^{31}P\{^1H\}$ NMR spectroscopy shows that the second alkene is replaced more rapidly than the first, even at low temperature. However, monosubstitution products can be isolated in some cases. At room temperature, acetonitrile and $SbPh_3$ form *cis*-[Ru(acac)$_2$(η^2-alkene)(L)], whereas ammonia, piperidine and pyridine give *trans*-[Ru(acac)$_2$(η^2-alkene)(L)]; the latter compounds are converted into the *cis*-isomers on heating.

In aromatic solvents, the second alkene of **2** is replaced more slowly than in THF. Addition of the bulky ligands PCy_3 or PPr^i_3 (1 equiv) to **2** in benzene gives *cis*-[Ru(acac)$_2$(η^2-C_2H_4)(L)] as yellow, air-sensitive solids, whose properties, structures and reactivities will be presented. The redox properties of the new compounds will also be discussed.



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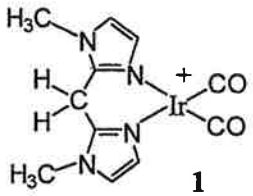
OP 11

CATIONIC METAL CATALYSTS WITH N-DONOR LIGANDS

Suzanne Burling, Leslie D. Field and Barbara A. Messerle and Linnea P. Soler

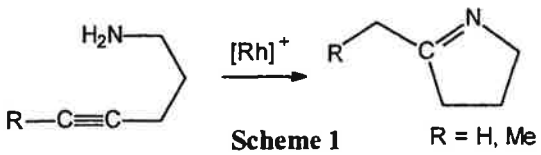
School of Chemistry, The University of NSW, NSW 2052, Australia
Email: b.messerle@unsw.edu.au

Organometallic complexes are widely used as catalysts for the synthesis of organic compounds. Cationic metal complexes of the form $[M(N\text{-}N)(CO)_2]^+$ *eg.* (**1**) [(N-N) = *bis*(*N*-methylimidazol-2-yl)methane or *bis*-pyrazolylmethane, M=Ir, Rh] act as effective catalysts for a range of reactions including the alcoholysis of silanes and the intramolecular cyclisation of alkynols and alkynoic acids to form oxygen containing heterocycles. We have found that {[Ir(*bis*-pyrazolylmethane)$(CO)_2$]BPh_4} catalyses not only the alcoholysis of silanes, but also the polymerisation of diols to form polysiloxane oligomers.



1

Compounds containing carbon-nitrogen (C-N) bonds are common in fine chemicals and industrial chemicals. Developing an efficient catalyst for the formation of C-N bonds *via* the addition of N-H bonds across unsaturated C-C bonds, hydroamination, is potentially a process of fundamental importance. The cationic Rh complex {[Rh(*bis*(*N*-methylimidazol-2-yl)methane)$(CO)_2$]BPh_4} (**2**) is an efficient catalyst for the intramolecular hydroamination of aliphatic as well as aromatic alkynes (*eg.* Scheme 1). We have investigated the mechanism of catalysed cyclisation with complex **2** using NMR spectroscopy. We have also determined the effect of specific counterions and ligand modifications on the efficiency of the catalyst.



Scheme 1

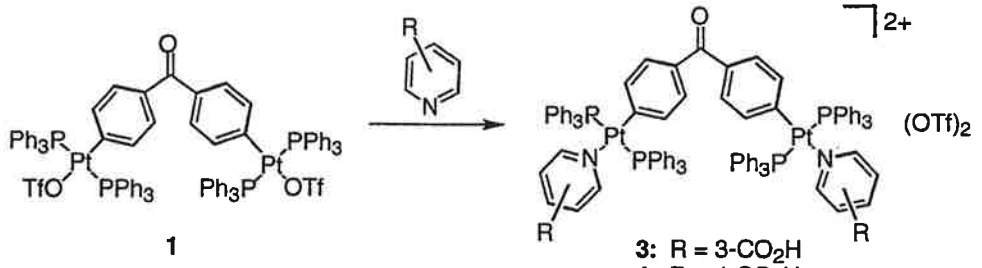
OP 12

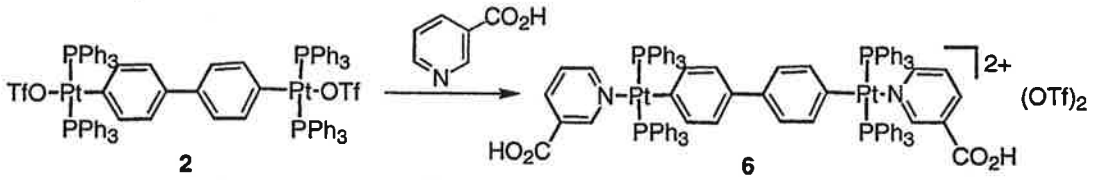
WITHDRAWN

NON-COVALENT ASSEMBLY OF MULTIMERIC PLATINUM MACROCYCLES

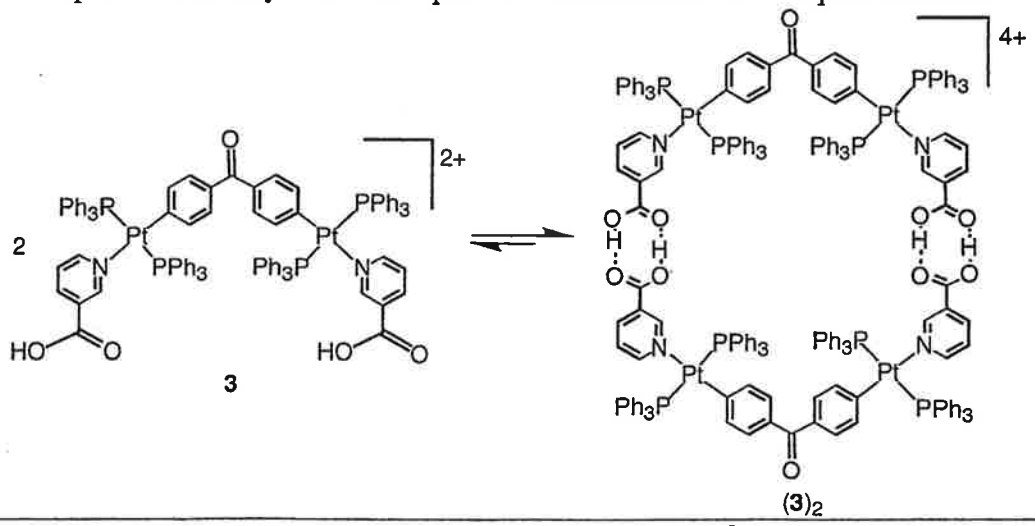
Michael G. Crisp, Nathan C. Gianneschi, and Louis M. Rendina
Department of Chemistry, The University of Adelaide, Adelaide, SA 5005.
lou.rendina@adelaide.edu.au

The use of the highly-directional H-bond as a means of controlling supramolecular aggregation is firmly established in the literature.[1,2] Recently, we commenced studies of the H-bond mediated assembly of discrete, macrocyclic entities containing platinum. To date, we have prepared and fully characterised a series of novel, dinuclear organoplatinum(II) complexes containing nicotinic acid **3** and **6**, *iso*nicotinic acid **4**, and nicotinamide **5**. We have also examined the non-covalent aggregation of these species in non-aqueous solution.





For complexes **3** and **6**, comprehensive ^{1}H NMR titration experiments were conducted under strictly anhydrous conditions in CD_2Cl_2 solution at 298 K. In both cases, the carboxylic acid O–H chemical shift was monitored as a function of monomer concentration, and the data were fitted to models for a *n*-merisation process according to the method of Saunders and Hyne.[3] For **3**, the titration data are consistent with the formation of a cationic, hydrogen-bonded macrocycle $(\mathbf{3})_2$ by spontaneous dimerisation at low concentrations. Similarly, the related biphenyl complex **6** appears to form a cyclic, hydrogen-bonded trimer $(\mathbf{6})_3$, as determined from the best-fit trimer model derived from the Saunders-Hyne analysis. This work demonstrates that the rational, non-covalent assembly of multimeric platinum macrocycles from simple monomers is feasible in non-aqueous solution.



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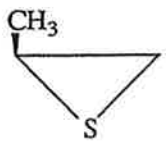
OP 14

Cyclic Thioethers as Ligands – Some Surprising Attachments

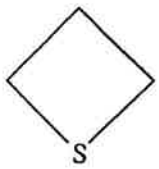
Ron S. Dickson, Qian-Qian Zhang, and Renuka Mayadunne

Department of Chemistry, Monash University,
Clayton, Victoria, Australia 3800
(ron.dickson@sci.monash.edu.au)

Strained ring thioethers such as propylene sulfide (**1**) and trimethylene sulfide (**2**) are potentially interesting ligands. However, in many of their reactions with metal species, (**1**) and (**2**) act as a source of sulfur through elimination of propylene or cyclopropane. In our search for compounds that might be a good source of epitaxial metal sulfides by chemical vapour deposition, we have isolated some interesting complexes of (**1**) and (**2**).



(**1**)



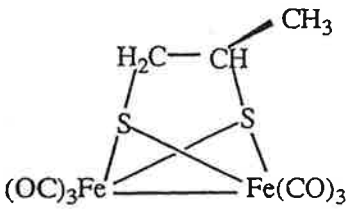
(**2**)

Treatment of pentacarbonyliron with trimethylamine – N – oxide followed by the addition of (**1**) yields the binuclear iron complex (**3**):

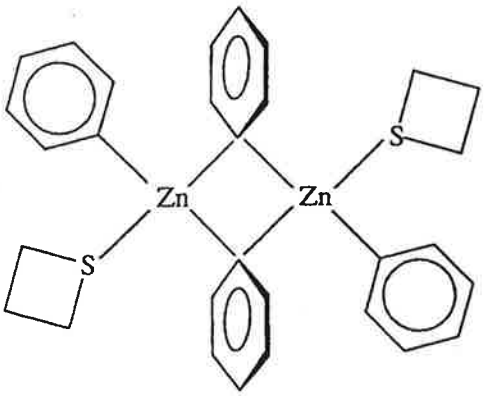
$$Fe(CO)_5 + (CH_3)_3NO + (1) \rightarrow Fe_2(CO)_6\{\mu - SCH(CH_3)CH_2S\} \quad (3)$$

Determination of the crystal structure of (**3**) revealed the formation of a new bridging ligand constructed from S and the ring-opened form of (**1**).

The reaction between diphenylzinc and (**2**) gave the dimeric product $[(C_6H_5)_2Zn(SCH_2CH_2CH_2)]_2$ (**4**). Determination of the crystal structure of (**4**) establishes that two phenyl groups occupy bridging position with the sulfur ligands in terminal locations.



(**3**)



(**4**)

DESIGNS OF MOLECULAR ARCHITECTURE USING CARBON CHAINS

OP 15

Michael I. Bruce, Ben Ellis, Ben C. Hall, Brian D. Kelly, Paul J. Low, Mark E. Smith, Natasha N. Zaitseva

Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005
Email: michael.bruce@adelaide.edu.au

Brian W. Skelton, Allan H. White

Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907

Karine Costuas, Jean-François Halet

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Université de Rennes 1, 35042 Rennes, France

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Recent results from the Adelaide group's exploration of the chemistry of metal complexes containing carbon chains of various lengths will be presented. These include

- Construction of molecular wires containing C_n strings linking two or more metal centres
- Building molecular squares and rectangles with metal corner pieces
- Using metal complexation to alter the geometry of links between metal centres
- Synthesis of highly unsaturated organic systems from metal complexes containing long carbon chains.

Our studies have led to the incorporation of both mono- and poly-metallic groups. The influence of different groups on the degree of electronic communication between the various metal centres will also be discussed.

OP 16

POLYMER SUPPORTED *N*-HETEROCYCLIC CARBENE COMPLEXES OF PALLADIUM: WELL-DEFINED, AIR-STABLE AND RECYCLABLE, HETEROGENEOUS CATALYSTS FOR THE *HECK* REACTION

Volker P.W. Bohm,[a] Michael G. Gardiner,[b] Manja Grosche[a], Wolfgang A. Herrmann,[a] Wolfgang Hieringer,[a] Gabriele Raudaschl-Sieber[a] and Jürgen Schwarz[a]

[a] Institut für Anorganische Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

[b] School of Chemistry, The University of Sydney, Sydney NSW 2006, Australia

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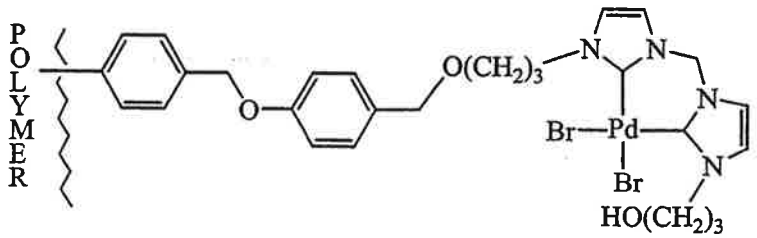
We have previously established chelating *N*-heterocyclic carbene complexes[1] of palladium(II) halides to be highly efficient homogeneous catalysts for the *Heck* reaction[2] and other carbon-carbon coupling reactions.[3] Our recently improved synthetic method for these types of complexes[4] has enabled the preparation of functionalised complexes allowing for their tethering to polystyrene supports for application in the heterogeneously catalysed *Heck* reaction. The catalyst system was chosen due to, (i) the high activity of the molecular catalyst in the homogeneously catalysed conversion of deactivated arylhalides, (ii) its stability under the reaction conditions commonly employed for the *Heck* reaction, and (iii) theoretical investigations that anticipated a low level of palladium leaching from the support.



We report our initial studies of these polymer grafted molecular catalysts for the *Heck* reaction, which are air-stable, recyclable and exhibit excellent activity towards activated and non-activated arylhalide substrates.

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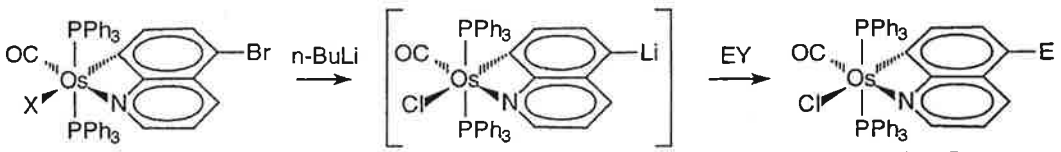
FUNCTIONALISATION OF σ-ARYL COMPLEXES OF RUTHENIUM AND OSMIUM

A. M. Clark, C. E. F. Rickard, W. R. Roper and L. J. Wright

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand.
e-mail: LJ.Wright@auckland.ac.nz

Although there are numerous examples of substituted σ-aryl complexes of transition metals, the functionality is almost invariably introduced to the organic fragment prior to its attachment to the metal. We are interested in studying substitution reactions of aryl groups already σ-bound to a transition metal since our preliminary work showed that a transition metal substituent can have a pronounced activating and directing effect on an aryl ligand. In addition to obtaining aryl ligands with unusual, or novel substitution patterns through this approach, suitably substituted transition metal - aryl complexes could in some cases serve as useful building blocks for more elaborate, metallated molecules.

A necessary condition for successful substitution reactions of this type is that the transition metal - carbon bond is sufficiently robust or unreactive to remain intact during the substitution reactions. The simple σ-phenyl complexes of ruthenium and osmium that we have studied do not always fulfil this requirement.[1] However, we have found that if the σ-aryl group is part of a chelate ring bound to the metal, treatment with very reactive reagents can be tolerated. As an example of this strategy we have found[2] that the η^2-8-quinolyl ligand bound to osmium in the complex Os(η^2-8-quinolyl)Cl(CO)(PPh_3)$_2$ (**1**) can be sequentially brominated, lithiated and then treated with a range of electrophiles to produce the corresponding substituted η^2-8-quinolyl ligands that bear alkyl, acyl, stannyl, carboxylate or aldehyde groups (see Scheme). The 2-(2'-pyridyl)phenyl ligand in the complex, Os(η^2-PyPh)Cl(CO)(PPh_3)$_2$ (**2**), can be similarly modified. The formyl-substituted product, Os(η^2-PyPh-4-CHO)Cl(CO)(PPh_3)$_2$ (**3**) which can also be conveniently prepared by direct formylation of (**2**) under Vilsmeier conditions, is a particularly useful building block for the synthesis of more elaborate molecules containing a metallated aryl function. For example, this aldehyde has been successfully condensed with a dipyrromethane to form a porphyrin in which the metallated aryl becomes one of the porphyrin *meso*-substituents. Further details of this product and the construction of other elaborate molecules from functionalised aryl ligands will be described.



E = *n*-Bu, Y = Br
E = $SnBu_3$, Y = Cl
E = C(O)Me, Y = NMe_2
E = C(O)H, Y = NMe_2

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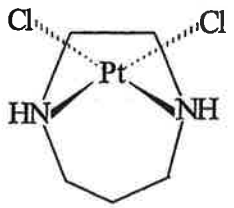
STERIC EFFECTS CAN INDUCE STEREOSPECIFIC PT/DNA BINDING

Vivienne P. Munk, Ronald R. Fenton, Trevor W. Hambley, Edwina C.H. Ling, Barbara A. Messerle[b]

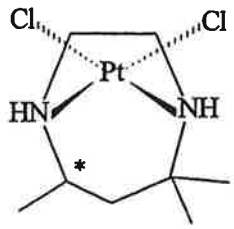
School of Chemistry, Building F11, University of Sydney, NSW 2006, Australia
[b] School of Chemistry, University of New South Wales, Sydney, NSW, 2052, Australia
e-mail : v.munk@chem.usyd.edu.au

The anti-cancer properties of cisplatin (*cis*-diamminedichloroplatinum(II)) are believed to derive from binding with DNA. Cisplatin can form a variety of adducts with DNA, including intrastrand and interstrand Pt-DNA adducts. However, which of the bifunctional adducts are responsible for the cytotoxic activity of cisplatin is unclear, as are the factors that control the adduct profile.

We have synthesised a series of bulky platinum complexes which are designed to be as likely as cisplatin to form interstrand adducts, but less likely to form intrastrand adducts. [Pt(1,4-diazacycloheptane)Cl_2] ([Pt(hpip)Cl_2]) was found to readily form interstrand GpG adducts, and not as readily form intrastrand GpG adducts. The [Pt(hpip)Cl_2] complex exhibited stereoselectivity in the formation of GpG adducts with salmon sperm DNA. HPLC and NMR investigations have shown that the two GpG adducts formed differ in the orientation of the ethylene and propylene chains. The propylene chain of [Pt(hpip)Cl_2] is more bulky, giving rise to unfavourable interactions with the exocyclic oxygen of the 3′ guanine. The isomer with the less bulky ethylene chain interacting with the exocyclic oxygen atom was preferred by a factor of 3.3:1. This led us to synthesise, resolve and investigate the biological activity of the platinum complex of a bulkier analogue of the hpip ligand, tmdz (tmdz=5,5,7-trimethyl-1,4-diazacycloheptane).



[Pt(hpip)Cl_2]



[Pt(tmdz)Cl_2]
* denotes a chiral carbon

Oligonucleotide binding studies have shown that the enantiomers of the [Pt(tmdz)Cl_2] complex shows an absolute preference for the formation of one isomer of the intrastrand [Pt(tmdz)d(GpG)] adduct, thus achieving stereospecific Pt/DNA binding. Enantioselectivity in adduct formation is also observed. 2D NMR studies of the adducts formed with GpG, to allow us to identify the isomer which is preferentially formed, are currently in progress.

CHROMATOGRAPHIC SEPARATION OF STEREOISOMERS OF HELICAL AND BIS(TRIDENTATE) COMPLEX SYSTEMS

OP 19

Bradley T. Patterson,[a] F. Richard Keene,[a] Gwénaël Rapenne,[b] Jean-Pierre Sauvage,[b] Torsten Kulke,[c] and Edwin C. Constable[c]

[a] *School of Biomedical and Molecular Sciences, James Cook University, Townsville, Queensland 4811, Australia*

[b] *Laboratoire de Chimie Organo-Minerale, Institut Le Bel, Université Louis Pasteur de Strasbourg, 4 rue Blaise Pascal, 67070 Strasbourg France*

[c] *Institut für Anorganische Chemie, Universität Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland*

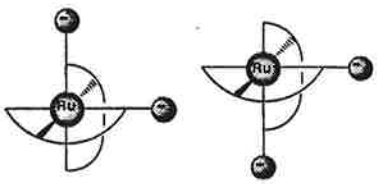
{E-Mail: Bradley.Patterson@jcu.edu.au}

We have recently developed a general cation-exchange chromatographic technique which has allowed the separation of stereoisomers of a wide range of mono- and oligonuclear complexes.[1-3] Invariably, the systems reported have involved tris(bidentate)-ruthenium(II) and -osmium(II) centres, but include separation of geometric isomers in mono- and di-nuclear complexes,[4,5] diastereoisomer separation in di- and tri-nuclear species,[6-9] and chiral resolution in mono-, di- and tri-nuclear complexes.[8,10]

The versatility of the method has now been demonstrated by its application to the separation of stereoisomers in two systems of different ligation characteristics.

1. A dinuclear double-stranded helix with iron(II) involving bis-2,2':6',2"-terpyridine {bis-terpy} ligand: a racemic mixture of the two helical forms was resolved into separate enantiomers.[11]

2. The octahedral bis(tridentate) $[M(tpy)_2]^{n+}$ centre is configurationally achiral. However, where tpy is unsymmetrically-substituted by a chiral group, the complex is rendered diastereoisomeric (for the homochiral ligation) or enantiomeric (for heterochiral ligation). In both cases for $[M(tpy\text{-}R)_2]^{n+}$ species, the separation was achieved using our technique.[12] Despite the lack of configurational asymmetry at the metal centre, significant Cotton effects were observed in absorption bands associated with MLCT metal-centred transitions.



The paper will discuss the separations and the nature of the observed interrelationship of the stereochemistry and physical characteristics of the two systems.

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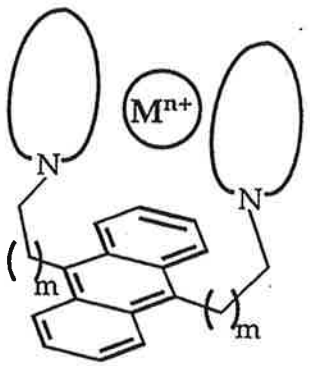
OP 20

Fluorescent Chemosensors for the Detection of Metal Ions.

Jason P. Geue, Nicholas J. Head, Stephen F. Lincoln, A. David Ward
Department of Chemistry, University of Adelaide, South Australia 5005
email: jgeue@chemistry.adelaide.edu.au

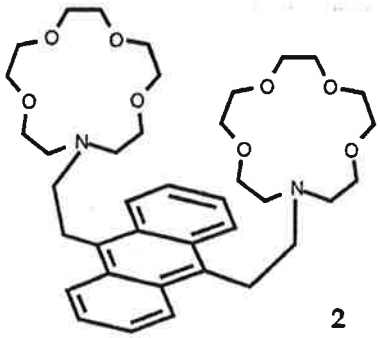
As part of a project whose aim is to develop new and sensitive methods for the determination of traces of metal cations in biological and environmental samples we are synthesising a range of chemosensors, with the general structure **1**, which consist of a fluorescent anthracene unit, alkyl linkers and two azacrown/ polyazacrown units for cation complexation.



1

m=1, 2

The sensors utilise Photo-induced Electron Transfer (PET) to signal cation binding. In the free ligand, PET occurs due to the proximate tertiary nitrogens (donors) in the azacrown deactivating the photoexcited fluorophore. When bound to a metal centre the donor electrons of the nitrogen atoms are no longer available to quench the excited state, resulting in a restoration of the natural fluorescence of anthracene. These principles have been successfully illustrated for system **2** which shows fluorescence enhancement with Ca^{2+} and Al^{3+} relative to K^+ and Mg^{2+} at equimolar metal ion concentrations. The synthesis of several other prototype sensors and their photophysical properties with a range of metal cations will be presented.



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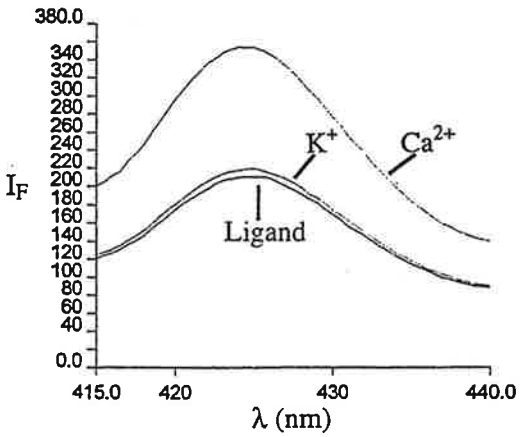


SEQUENCE SELECTIVITY OF CISPLATIN: 1,2- AND 1,3- INTRASTRAND AND 1,2-INTERSTRAND BINDING KINETICS OF CISPLATIN TO DNA.

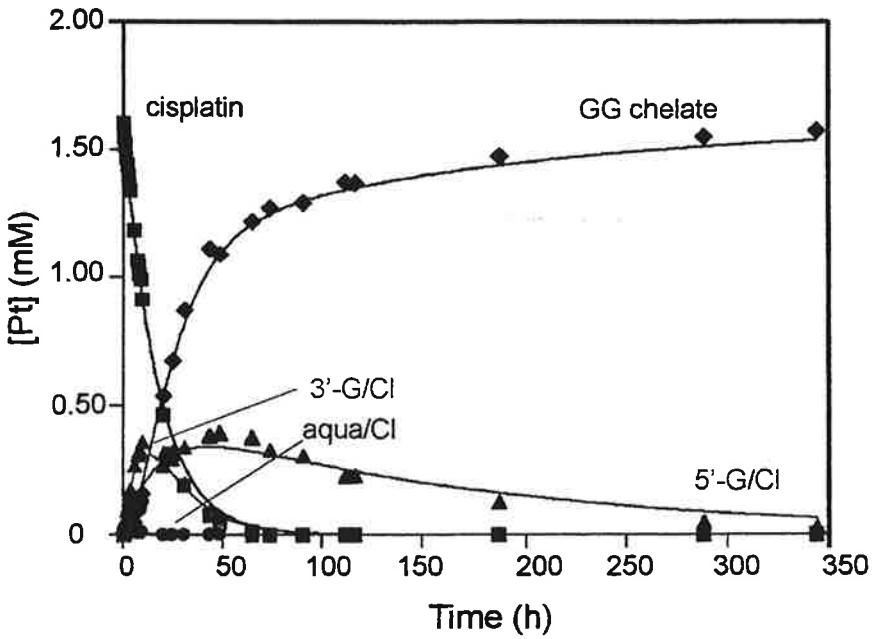
Trevor W. Hambley[†], Murray S. Davies[†,‡] and Susan J. Berners-Price[‡]

[†]. School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia
[‡]. School of Science, Griffith University, Brisbane, QLD 4111, Australia
email. t.hambley@chem.usyd.edu.au

Cisplatin, *cis*-$[PtCl_2(NH_3)_2]$ is believed to afford its anticancer properties by binding to intracellular DNA, which brings about a change in the DNA conformation. Platination is concentrated at intrastrand GpG (~65%) and ApG (~25%) sites, and is also seen at low levels at intrastrand GpNpG and interstrand GG positions. Bifunctional binding is not observed at intrastrand GpA sites.

We have reported the binding kinetics of cisplatin to 14- base pair oligonucleotides bearing ApG and GpA sites, and recently with a GpG site using [^{1}H,^{15}N] HSQC 2D NMR spectroscopy.[1-3] Our results have shown that monofunctional formation at GpA is slowed relative to ApG and that the rate of closure from the 5' base is an order of magnitude slower than from the 3' side, irrespective of the bases involved.

We have extended the studies to include binding to oligonucleotides where the sequences have been selected to afford bifunctional GG interstrand crosslinks, differing only in the direction of the crosslink, and to a duplex with a GpTpG intrastrand binding site. The formation of monofunctional rotamer species at some sequences is discussed, and the influence of the rates of platination on the product distribution is explored.



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OP 22

The Influence of the Non-Leaving Groups on the Lipophilicity and the Pharmacological Properties of Some cis-Platinum(II) Complexes

Jean-Pierre Souchard[a], Franz Wimmer[b], Tam T.B. Ha[c] and Suzi Cros[d]

a. Laboratoire de Ciblage en Thérapeutique, 35 Ch. des Maraîchers, 31062 Toulouse, France.
b. Department of Chemistry, Universiti Brunei Darussalam, BE1411, Brunei.
c. Laboratoire de Chimie Inorganique, Université Paul Sabatier, 180 route de Narbonne, 31062 Toulouse, France.
d. Institut de Pharmacologie et de Biologie Structurale du CNRS, 205 route de Narbonne, 31077 Toulouse, France.

Email: fwimmer@ubd.edu.bn

Platinum compounds with antitumor activity are generally neutral. However, a few charged *cis*-diaminediaquaplatinum(II) complexes have been reported to have antitumor activity against murine models. In order to understand the basis of this activity, we have compared the physicochemical property hydrophobicity and the pharmacological activities (growth inhibition, toxicity, antitumor activity) of some diaqua {*cis*-$[Pt(A)_2(H_2O)_2]^{2+}$, $2NO_3^-$} and dichloro *cis*-$[Pt(A)_2Cl_2]$ platinum complexes (A = NH_3, aliphatic amine, substituted pyridine).

Murine toxicity and antitumor activity of the diaqua complexes toward P388 leukemia were modulated by the nature of the non-leaving group. The amine diaqua compounds showed good antitumor activity while the pyridine diaqua complexes were inactive. The partition coefficient, log P ([octanol]/[water]), of the compounds correlates with the antitumor activity and the toxicity of both neutral dichloro and charged diaqua complexes with aliphatic amine or NH_3 ligands. For these compounds we propose an activity window based on the partition coefficient.

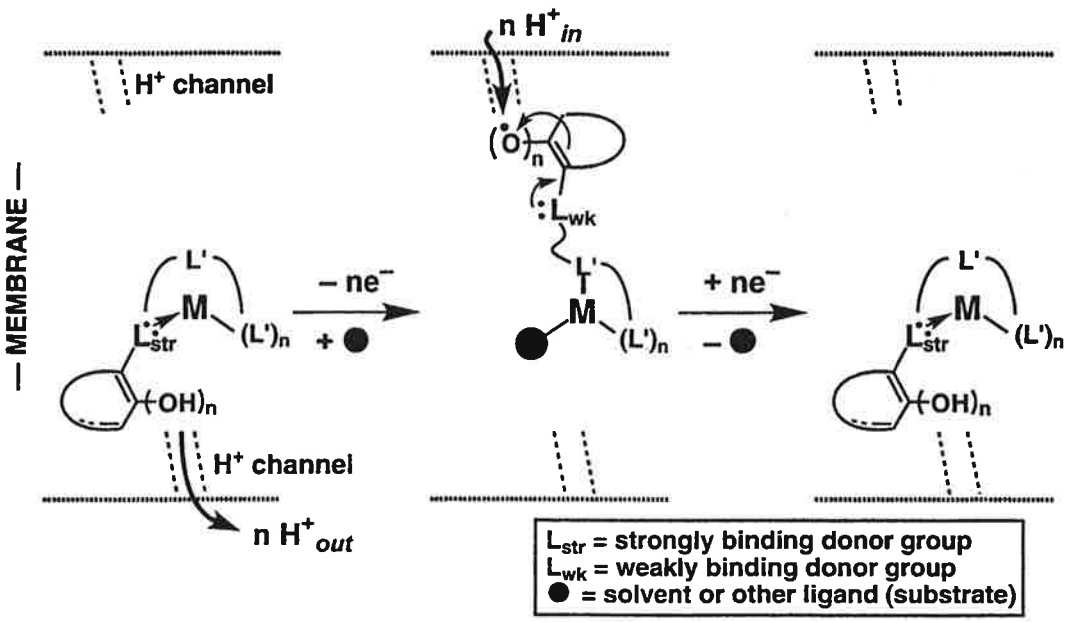
Proton-coupled redox-switchable hemilability as a basis for conformational proton-pumping at a transition metal centre

Stephen B. Colbran and Zhicong He

School of Chemistry, University of New South Wales, Sydney, 2052, Australia

s.colbran@unsw.edu.au

"Proton pumps" translocate protons in opposition to a proton gradient. Examples include those proteins of the respiratory and photosynthetic chains which couple the reactions they catalyse to proton pumping through the protein and across a membrane. We propose a new mechanism for a proton pump based on a transition metal complex of a redox-switchable hemilabile ligand (RHL)[1-3] where the ligand redox-switch is a proton-dependent redox couple. Binding of the RHL to the metal centre is modulated by the ligand redox switch. Proton uptake and release occurs in discreet conformational states, one for input and one for output of electrons and protons, leading to vectorial proton pumping as depicted diagramatically below. Model studies of copper complexes demonstrating "proof-of-concept" will be described and possible implications suggested for proton pumping by heme-copper oxidases such as cytochrome c oxidase, the terminal protein of the aerobic respiratory electron-transfer chain.



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Homochiral Group 1 Amides : Synthesis, Structure and Aza-Allyl Formation

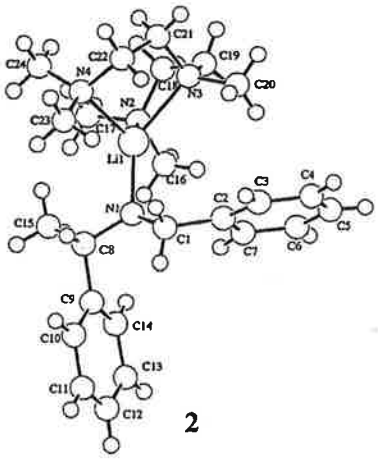
Phil Andrews, Peter Duggan, Gary Fallon and Anna Peatt

Department of Chemistry, Monash University, Melbourne. Vic. 3168.
Email : p.andrews@sci.monash.edu.au

Homochiral lithium amides have played a prominent role in asymmetric synthesis for over a decade now.[1] In particular they have been found to be useful in highly selective deprotonations of prochiral substrates, eg ketones, in the enantioselective rearrangement of epoxides to allylic alcohols and in stereoselective 1, 2 conjugate addition reactions. High selectivity is often promoted by the use of Lewis base donors such as THF, HMPA and (-)-sparteine.

We have been particularly interested in the chiral amine, (S) (α-methylbenzyl)benzylamide, **1**, which has found extensive use in the synthesis of β-amino acid derivatives from its addition to α, β- unsaturated esters. [2] In order to understand the selectivity and reactivity, and to control these factors, it is important to understand the solution state structure of the lithium amide Often the solid state structure can be the most reliable guide to knowing what is present in solution. Although the solid state structures of achiral group 1 amides have been extensively investigated surprisingly there is still very little structural information on their chiral counterparts.[3]

Therefore, we have undertaken a solid state study of the group 1 complexes of **1**. In doing so we have obtained several crystal structures of Li complexes, **2**, but have also shown that the use of Na or K forces conversion to aza-allyl products *via* H_2 or MeH elimination from the benzylic protons, **3**. A comparative study with dibenzylamine will be presented.



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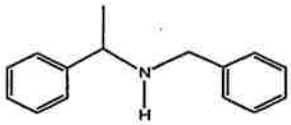

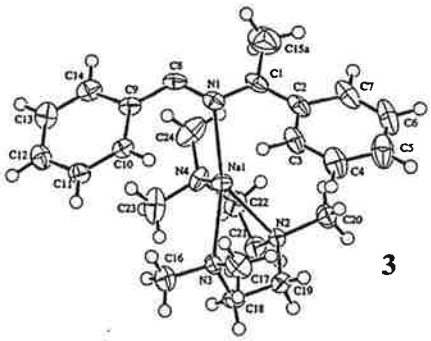

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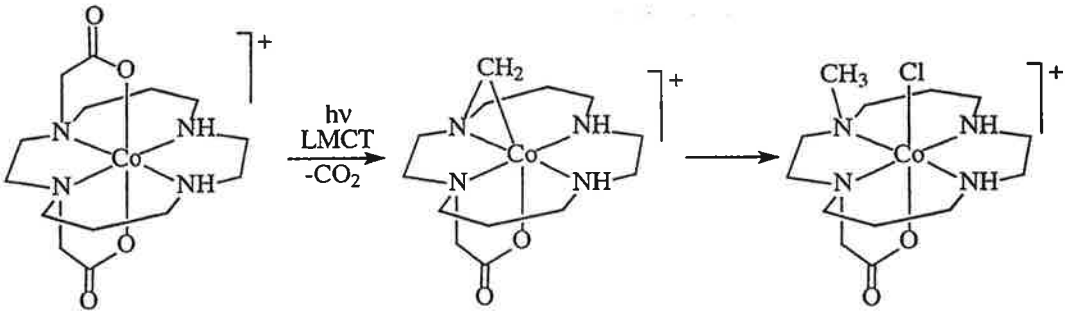
FORMATION OF A PENDANT-ARM CYCLAM LIGAND BY INTRAMOLECULAR ALKYLATION REACTIONS ON A COBALT(III) COMPLEX: COORDINATION CHEMISTRY AND PHOTODECARBOXYLATION TO GIVE A Co-C-N THREE-MEMBERED RING

Deborah M Tonei, David C Ware, Penelope J Brothers and George R Clark

Department of Chemistry, The University of Auckland, Private Bag 92019,
Auckland, New Zealand.
p.brothers@auckland.ac.nz

Condensation reactions of coordinated amines constitute a class of reaction which has generated a wealth of new ligands and interesting chemistry. In contrast, template alkylation reactions are less well known. We have recently developed cobalt(III) mixed ligand systems which are predisposed for intramolecular alkylation. The complexes contain amine ligands bearing N-chloroalkyl substituents which act as intramolecular alkylating agents, forming new cobalt(III) complexes of acyclic and macrocyclic hexadentate ligands. One example is the cyclam derivative 1,4-BCC illustrated below.[1] The cobalt(III) centre in $[Co(1,4\text{-}BCC)]^+$ can be reduced to form an isolable cobalt(II) complex containing the same ligand. Both the Co^{III} and Co^{II} complexes have been structurally characterised. The Co^{III}/Co^{II} couple is electrochemically reversible in H_2O.

Photochemical decarboxylation of $[Co(1,4\text{-}BCC)]^+$ generates a complex, $[Co(L^1)]^+$, which incorporates a three-membered chelate ring containing a Co-C σ-bond.[2] The three-membered ring can be opened using HCl to give a complex bearing an N-methyl group on the cyclam-derived ligand, $[CoCl(L^2)]^+$. We have extended this chemistry to a series of related macrocycles which also undergo photochemical decarboxylation to give Co-C-N three-membered chelate rings. Kinetic stabilisation of the strained rings is attributed to their incorporation into the larger macrocycles.



$[Co(1,4\text{-}BCC)]^+$ $[Co(L^1)]^+$ $[CoCl(L^2)]^+$

We have recently developed a procedure for demetallating $[Co(1,4\text{-}BCC)]^+$ to yield the free $H_2(1,4\text{-}BCC)$ ligand, and consequently we have been able to explore its coordination chemistry with other metals. Structural characterisation of the Cu^{II}, Zn^{II} and Cr^{III} complexes shows, as expected, coordination of the metals within the cyclam moiety. However, in two of the complexes coordination of addition metal ions (Zn or Cu) to the carboxylate oxygen atoms links the complexes into chains. Intriguing differences between the modes of coordination to the carboxylate oxygen atoms are noted.

Details of the synthesis and structural and spectroscopic characterisation of all the new complexes will be presented.

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OP 26

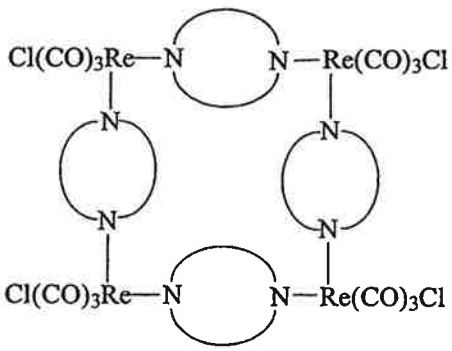
SYNTHESIS AND VIBRATIONAL SPECTROSCOPY OF NEW SWITCHABLE ORGANOMETALLIC MOLECULAR BOXES

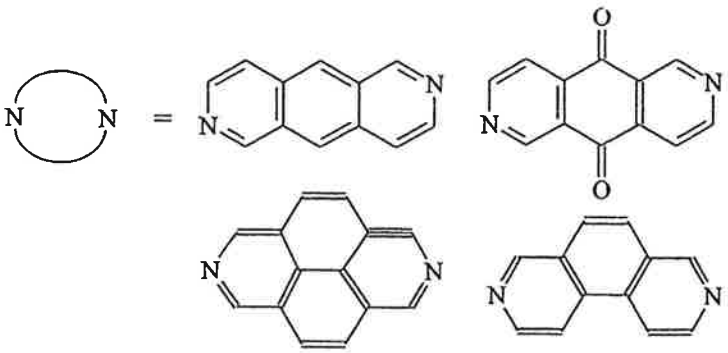
JOY L. KERR, KEITH C. GORDON, HENRIK G. KJAERGAARD, BRIAN H. ROBINSON and JIM SIMPSON

Department of Chemistry, University of Otago, PO Box 56, New Zealand

Email: brobinson@alkali.otago.ac.nz

A number of systems have been synthesized in order to explore the fundamental constraints which determine the excited states of coupled organometallic fluorophores and electrophores. In this paper we describe the synthesis and electrochemistry of molecular boxes and their precursors where the fluorophore is both aromatic and rhenium(I) and the electrophore is an organometallic. The IR and Raman spectra of the ligands and the metal complexes have also been measured. Frequencies and intensities of the ligand spectra, calculated using the Hartree-Fock and Density Functional Theory and a 6-31G(d) basis set, were in good agreement with experimental data.





OP 27

Bimetallic Reactivity

B. Bosnich
Department of Chemistry, The University of Chicago
5735 South Ellis Avenue
Chicago, Illinois 60637
bos5@midway.uchicago.edu

It is found that, in bimetallic systems formed by binucleating ligands, the oxidation of one metal leads to the deactivation of the other to oxidation. This mutual deactivation appears to be controlled mainly by mechanical coupling where the conformational ligand changes engendered by oxidation of the first leads to deactivation of the second metal to oxidation. Various new ligand systems will be presented which may obviate this mechanical deactivation. The relevance of the work to cooperative multimetallic reactivity in biological systems will be discussed.

Metal Enzyme Models Featuring Mono- and Di-thiolate Ligands. Importance of NH...S Bonding for the Reactivity Control

Akira Nakamura
Dept. Chemistry, Toho University, 2-2-1 Miyama, Funabashi, Chiba, Japan 274-8510; anaka@chem. sci.osaka-u.ac.jp

Enzymatic activity for electron transfer and redox reaction of many known redox enzymes is based on one-electron redox processes at the transition metal center coordinated by thiolate ligand(s). During our continued study of these enzyme models, we have found that these functions are delicately controlled by the NH...S hydrogen bond(s) at the coordinating thiolate(s). Our detailed research on the cysteine-containing oligo-peptide ligands and on the *ortho*-acylaminobenzenethiolato ligands indicated remarkable modification of the redox properties by the strategic hydrogen bond(s).

For example, the resting Fe(III) state of the well-known P-450 enzymes has been found to be stabilized by the NH...S hydrogen bonds at the axial cysteine-thiolate ligand. The hydrogen bonding thus controls the ionicity of the Fe-S bond and also the dioxygen activation at the other side of the heme plane. Specific sequences of coordinating oligo-peptides are very important for the stability of hydrogen bonds at the thiolate.

Thus, a systematic spectroscopic study of the tetra- and larger peptide complexes of $[Fe^{III}(OEP)]^+$ (OEP; octaethylporphyrinato) in solution revealed that presence of a specific turn peptide conformation and and of an α-helix following it greatly enhances formation of the NH...S hydrogen bond and thus stabilizes the resting state of the enzyme[1]. Transition metal complexes of *ortho*-acylaminobenzenethiolates designed to have similar hydrogen bonds were found to have positively shifted redox potentials[2].

Similarly, *ortho*-acylaminobenzenedithiolato complexes of Mo(VI) as the models of Mo- and W-oxidases, such as DMSO-oxidase and aldehyde-ferredoxin reductase, are prepared and their O-atom transfer reactivities are investigated to reveal their excellency as the model where the reactivity is also controlled by the NH···S hydrogen bonding.

Reference: 1)T.Ueno, Y.Kousumi, K.Yoshizawa-Kumagaye, K.Nakajima, N.Ueyama, T-a.Okamura, A.Nakamura, *J. Am. Chem. Soc.*, **120**, 12264(1998). 2) T-a.Okamura, S. Takamizawa, N. Ueyama, A. Nakamura, *Inorg. Chem.*, **37**, 18(1998).

OP 29

BORYL COMPLEXES OF RUTHENIUM AND OSMIUM

G. R. Clark, G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, and L. J. Wright

Department of Chemistry, The University of Auckland, Private Bag 92019
Auckland, New Zealand

e-mail: w.roper@auckland.ac.nz

Oxidative addition processes involving the breaking of B-H or B-B bonds at Ru or Os centres in suitable low oxidation state complexes have given access to a large number of stable boryl complexes. Some typical examples are the following: $[Os(Bcat)Cl(CO)(PPh_3)_2]$, $[Ru(Bcat)_2(CO)(CNR)(PPh_3)_2]$, $[Os(BCl_2)Cl(CO)(PPh_3)_2]$, and $[Os[B(OEt)_2]Cl(CO)(PPh_3)_2]$. This lecture will focus attention on three aspects of this work.

(1) Systematic structural studies reveal trends in M-B bond distances as changes are made to the heteroatoms present on boron, or to the accompanying ligands especially those ligands trans to the boryl ligand. The observed trends can be accommodated by attributing not only good σ-bonding capability to boryl ligands, but also, at least in some cases, good π-acceptor capability.

(2) Complexes which are good models for postulated intermediates in either metal-catalysed hydroboration processes or the metal-catalysed borylation of arenes have been characterised. Specifically, the syntheses and reactions of cis- and trans- $[Os(Bcat)(o\text{-tolyl})(CO)_2(PPh_3)_2]$ will be described.

(3) Reactions can occur at the boron centre without cleavage of M-B bonds. Most of these reactions involve the BCl_2 ligand which undergoes reactions forming new boryl ligands with B-O or B-N bonds and in some cases base-stabilised borylene complexes.

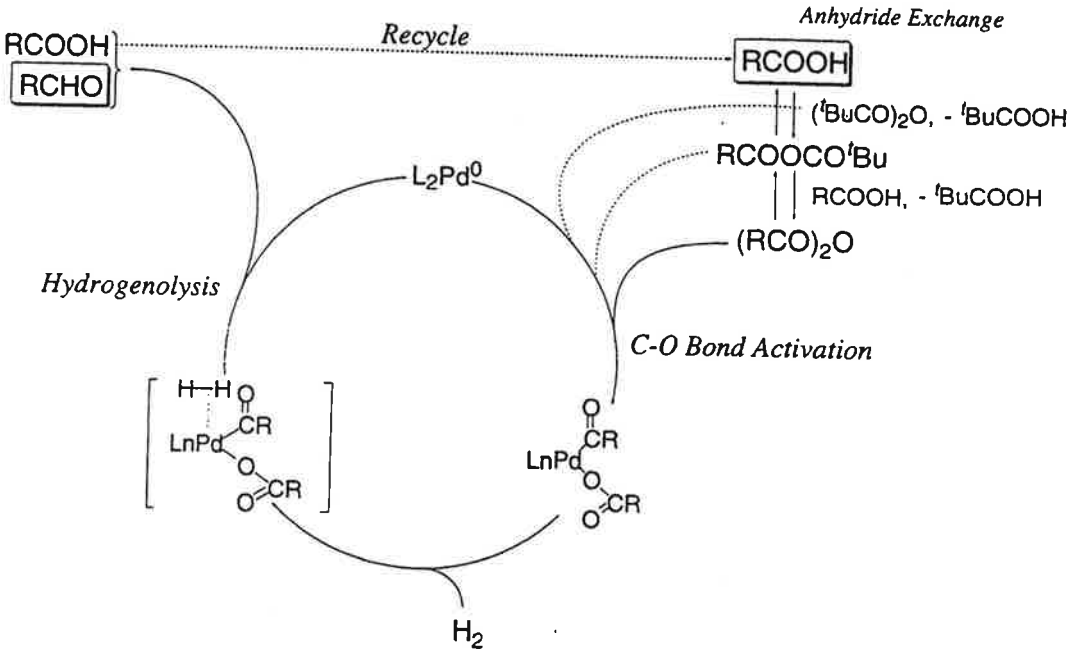
Development of Palladium-Catalyzed Halide-Free Catalytic Processes

OP 30

Akio Yamamoto, Kazuhiro Nagayama, and I. Shimizu

Department of Applied Chemistry, School of Science and Engineering
Waseda University, Shinjuku, Tokyo 169-8555, Japan
e-mail: akioyama@mn.waseda.ac.jp

Most of the palladium-catalyzed coupling processes employ organic halides as the starting material utilizing the ability of the halides oxidatively adding to a Pd(0) complex and of the high reactivity of the organopalladium complexes thus generated. The halide ion, however, should be eventually removed with aid of a base to produce the end product. Thus development of a halide-free process is desirable from the view point of atom economy and for avoiding the waste production. In our fundamental studies to examine the oxidative addition of oxygen-containing organic compounds to Pd(0) complexes we found among others oxidative addition of carboxylic anhydrides to palladium(0) complexes to give acyl(carboxylato)bis(tertiary phosphine)palladium complexes [1,Ê2]. On the basis of our studies on the reactivities of the acyl(carboxylato)palladium complexes we have developed a novel catalytic process to convert carboxylic acids directly into aldehydes. The essential feature of the catalytic mechanism can be expressed by the scheme shown below. The detail of the mechanism and the scope of the applications will be presented.



Ref. 1) K. Nagayama, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc., Jpn.* **72**. 573 (1999)
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Oxometalates as Specific Organic Oxidation Catalysts

A. J. Bailey, W. P. Griffith* and M. Suriaatmaja 28 September 1999

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

*w.griffith@ic.ac.uk

We have long been interested in the use of oxoruthenates[1] and oxo-osmates[2] as catalysts for specific organic oxidations, and present here new data on the use of environmentally friendly co-oxidants - ozone, H_2O_2 and perhydrates - with such catalysts as well as other recently developed oxidation systems.

Ozone reacts[3] with $RuCl_3.nH_2O$ to give the trigonal bipyramidal ruthenate, *trans*-$[Ru(OH)_2O_3]^{2-}$; with *trans*-$[OsO_2(OH)_4]^{2-}$ it gives perosmate, *cis*- $[Os(OH)_2O_4]^{2-}$. These can be used for the oxidation of primary alcohols to aldehydes, or carboxylic acids; secondary alcohols to ketones and primary amines to nitriles. The use of Fe(TMP)Cl as a catalyst for the epoxidation of alkens with O_3 as co-oxidant has been developed[4]- an unusual reaction since O_3 is an effective alkene cleavage reagent.

We find that H_2O_2 is an effective co-oxidant with $RuCl_3.nH_2O$ as catalyst, in the presence of phase-transfer catalysts, for the oxidation of primary alcohols to aldehydes or carboxylic acids or secondary alcohols to ketones, and have optimised earlier[5] observations on this topic. The more convenient and portable perhydrates sodium peroxoborate, $Na_2[(B_2(O_2)_2(OH)_4].6H_2O$ and sodium carbonate perhydrate, $Na_2CO_3.1.5H_2O_2$ can be similarly used. Data are presented on the use of RuO_4 (generated from $RuCl_3.nH_2O$ and $IO(OH)_5$) in water-acetonitrile for the oxidative cleavage of alkenes and alkynes to carboxylic acids wuth periodic acid as co-oxidant, and on the use of *trans*-$[Ru(OH)_2O_3]^{2-}$ with persulfate as co-oxidant for the oxidative dehydrogenation of amines to nitriles.

Raman spectroscopy has been used to study the nature of catalytic intermediates in some of these reactions.

Acknowledgements We thank Johnson, Matthey for loans of ruthenium and osmium chemicals, and Air Products and Chemicals Inc. for a postdoctoral grant to A.J. B.

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2. A. J. Bailey, M. G. Bhowon, W. P. Griffith, A. G. F. Shoair, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 3245 aand refs. therein.
3. A. J. Bailey, W. P. Griffith, S. P. Marsden, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1998, 3673.
4. A. J. Bailey, W. P. Griffith, S. M Marsden, E. H. Smith and F. Waller, *J. Mol. Cat.* in press.
5. G. Barak, J. Dakka and Y. Sasson, *J. Org. Chem.* 1988, **53**, 3553;W. C. Frank, M. S. Neff and M. S. Pavlin, *Prog. Inorg. Chem. (Gif)* 1986, 75;

OP 32

MY SMALL CONTRIBUTION TO ARENE RUTHENIUM CHEMISTRY - A BENNETT CONNECTION-

Lai Yoong Goh
Department of Chemistry
National University of Singapore, Kent Ridge, Singapore 119260.
email: chmgohly@nus.edu.sg

The paper will deal with the chemistry of some hexamethylbenzene ruthenium(II) complexes, with emphasis on those containing cyclic and acylic polythiaether ligands.

LINEAR TETRANUCLEAR Pd-Mo-Mo-Pd COMPLEXES WITH PALLADIUM IN THREE OXIDATION STATES, Pd(0), Pd(I), and Pd(II)

KAZUSHI MASHIMA

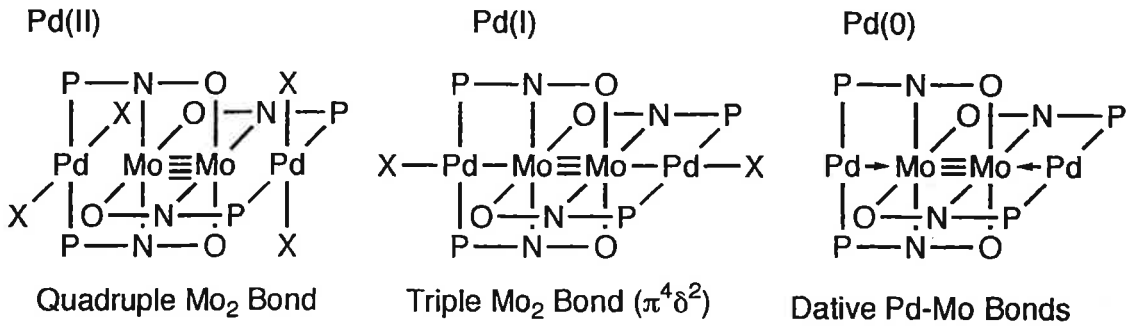
Department of Chemistry, Graduate School of Engineering Science,

Osaka University, Toyonaka, Osaka 560-8531, Japan

E-mail: mashima@chem.es.osaka-u.ac.jp

Many complexes bearing a multiple metal-metal bond have been prepared and their structure and bonding have been realized. The addition of metal to axial positions of multiple metal-metal bond forming the linearly arranged tetranuclear cluster complex had not been investigated, though many examples exist for the coordination of donor ligands to the axial positions of metal-to-metal complexes. Thus, we prepared straight linear tetranuclear complexes by using pyphos ligand (pyphos = 6-diphenylphosphino-2-pyridonate), which has unique coordinating sites comprised of three kinds of elements, *i.e.* phosphine, nitrogen and oxygen atoms, in almost linear fashion.

Treatment of $Mo_2(pyphos)_4$ (**1**) with Pd(II) complexes afforded tetranuclear complexes of the general formula, $Mo_2Pd_2X_4(pyphos)_4$ (**2**) (**a**: X = Cl; **b**: X = Br; **c**: X = I), which have quadruply-bonded Mo_2 core and no bonding between a Pd(II) atom and a Mo atom. Treatment of **2** with reducing reagents, photoirradiation, or thermal reduction resulted in the formation of metal-metal bonded tetranuclear complexes $Mo_2Pd_2X_2(pyphos)_4$ (**3**) (**a**: X = Cl; **b**: X = Br; **c**: X = I), respectively. Further reduction of **3** afforded a Pd(0) complex $Mo_2Pd_2(pyphos)_4$ (**4**), whose Pd(0) center reacted with dichloromethane to form $Mo_2Pd_2(CH_2Cl)_2Cl_2(pyphos)_4$ (**5**). Structural features and reactivities of **2**—**4** will be discussed.



Synthesis of New Sulfur-Containing Cyclic Ligands at Dinuclear Metal Centres

John E. Davies, Louisa J. Hope, **Martin J. Mays**, Peter K. Tompkin and Anthony D.Woods, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom. e-mail: mjm14@cam.ac.uk

New reactions describing different ways of incorporating sulfur into cyclic ligands by the activation of small molecules at dinuclear transition metal centres will be described. Thus the reaction of Ph_2SPh with mixed-metal Co/Mo or Co/W complexes containing bridging alkyne ligands, RCCR, leads to four-membered metallacyclic ligands of the type M-P-C=C or M-S-C=C where M can be Co or Mo/W depending on the nature of R and the reaction conditions.

Five-membered sulfacyclic rings of the type MP_2S_2C are obtained when CS_2 is reacted with the P_2- bridged complex $[(C_5H_5)_2Mo_2(P_2)(CO)_4]$

A further series of sulfacyclic ligands containing much larger rings can be obtained from the reactions of coordinated dialkynes with thiols. By this means we have synthesised sulfacyclic ligands containing rings with up to four sulfur atoms and sixteen carbon atoms. The structures of the new complexes will be presented and the reaction pathways leading to their formation will be discussed

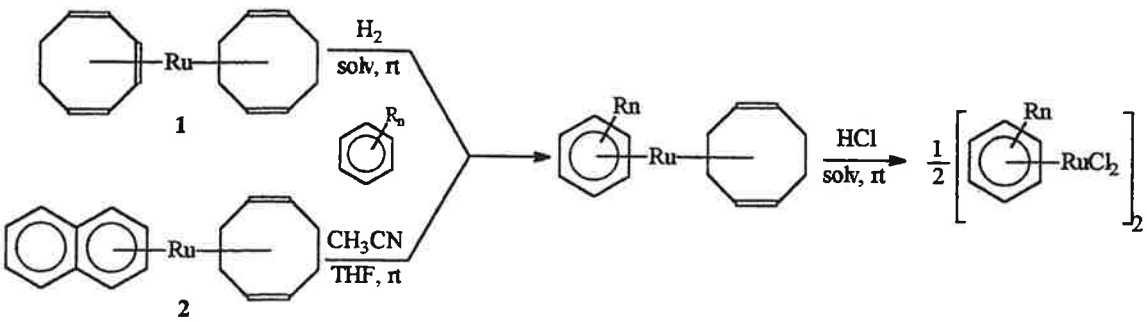
Ruthenium(0) Complexes as Precursors of Homogeneous and Heterogeneous Catalysts

OP 35

Paolo Pertici

Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa (Italy). E-mail: pervit@dcci.unipi.it

The discovery of new and more efficient synthetic pathways to prepare reactive transition metal complexes has played a crucial role in the development of preparative chemistry and catalysis. In this frame, the ruthenium(0) complexes $Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})$, **1** [$C_8H_{10}$ = cycloocta-1,3,5-triene; C_8H_{12} = cycloocta-1,5-diene] and $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$, **2** [$C_{10}H_8$ = naphthalene], available by simple procedures [1,2], are valuable starting materials very useful for extending the ruthenium chemistry. They contain organic ligands that can be easily displaced from the metal leaving coordination sites more accessible to the reagents. For this reason, complexes **1** and **2** exhibit a particular reactivity; as an example, they react with aromatic compounds, under mild conditions, giving the complexes $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ that are precursors of the widely employed $[RuCl_2(\eta^6\text{-arene})]_2$ compounds (Scheme) [1,2].



Scheme

Complexes **1** and **2** are of relevance in catalysis. The results obtained using these complexes as homogeneous catalytic precursors in the isomerisation, hydrogenation and oligomerisation of unsaturated substrates will be presented. In addition, the use of **1** and **2** as source of supported and unsupported ruthenium metal nanoparticles to prepare heterogeneous catalysts will be discussed.

[1] P. Pertici, G. Vitulli, *Comments Inorg. Chem.*, 11 (1991) 175 and references therein.

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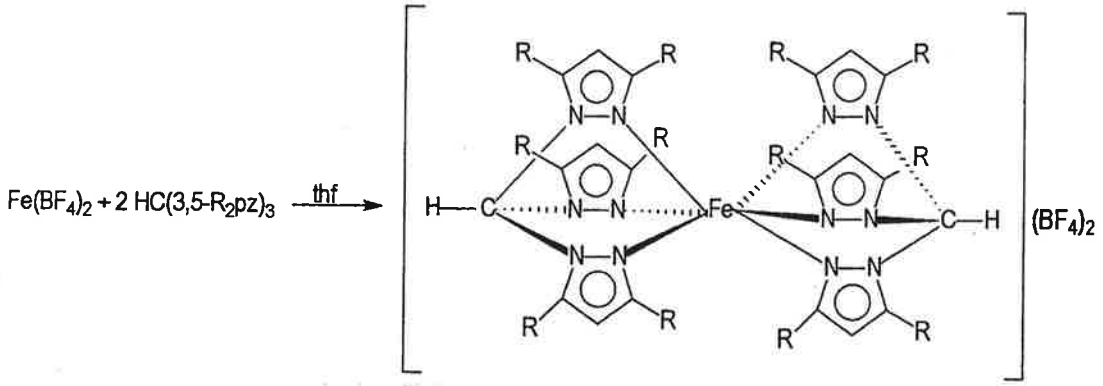
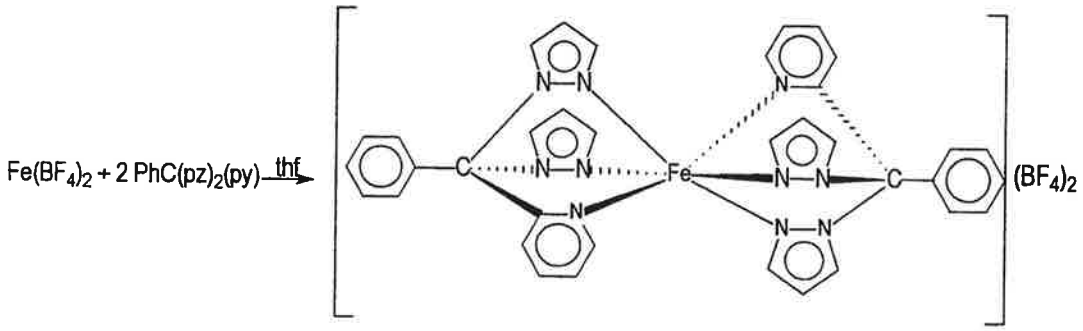
TRIS(PYRAZOLYL)METHANE LIGANDS: SYNTHESES OF IRON(II) COMPLEXES WITH UNUSUAL MAGNETIC PROPERTIES

Daniel L. Reger, Christine A. Little and T. Christian Grattan
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, 29208, USA, Reger@psc.sc.edu.

Tris(pyrazolyl)methane and related ligands such as $PhC(pz_2py)$ (pz = pyrazolyl, py = pyridyl) have been used in the syntheses of cationic iron(II) complexes.



R=H (purple) **1**
R=Me (white) **2**



(red) **3**

Complex **1** is diamagnetic in the solid state. A crystal structure of this compound shows the iron in an octahedral arrangement with an average Fe-N distance of 1.97 Å, as expected for low spin Fe(II). In solution, complex **1** is undergoing a high spin/low spin equilibrium, with the amount of the high spin form increasing with increasing temperature of the solution. Complex **3**, utilizing the new ligand $PhC(pz_2py)$, is diamagnetic in both the solid state (average Fe-N distance of 1.96 Å) and in solution. In contrast, complex **2** is high spin, with an octahedral structure and Fe-N average distance of 2.17 Å. Clear crystals of **2** turn purple below 200 K. At this temperature the molar susceptibility of the solid lowers abruptly, but follows Curie behvior at lower temperatures. Mössbauer studies show that the solid reversibley changes from high spin to about a even mixture of high and low spin over a very small temperature range.

Floating Inorganic Chemistry without a Solvent:
Gas Phase Coordination Chemistry in a Mass Spectrometer

Keith J. Fisher, Ian G. Dance and Gary D. Willett
School of Chemistry, University of New South Wales, Sydney, NSW 2052.

The gas phase is just another phase and as in the condensed phases, coordination chemistry is possible, observable and measurable.

Where can we find a metal species with a coordination number of zero? In the gas phase, in a mass spectrometer as M^+ or M^-.

The gas phase is where metal coordination numbers of zero to six (possibly greater than six) can occur, be observed and even reacted. Metal complexes approaching the complexity of condensed phase systems may be produced in the gas phase, albeit in very low concentrations.

A review of gas phase metal coordination gives us some idea of the scope of this chemistry. Using mass spectrometric techniques, only ionic species may be observed but both anions and cations may be studied; there are even ways to study neutral molecules.

The coordination number of a metal is a useful parameter to use in discussing gas phase species.

Coordination number 1 is often observed in the gas phase with ions such as VO^+, LaC_2^+ $AuXe^+$.

Coordination number 2 (even known in the condensed phase) is quite common in the gas phase with examples such as NiS_2^-, $M(H_2O)_2^+$ and $Ag(C_6H_5SH)_2^+$.

Coordination number 3 is also known in the condensed phase and is quite common in the gas phase e.g. VO_3^-,

Reactivity in the gas phase decreases markedly as the coordination number becomes greater than 3 but with the advent of soft ionization techniques such as electrospray many metal complexes may be observed with metal coordination numbers of four or greater. Are they reactive?

This presentation will use examples from our research and the work of others to introduce this less studied area of Coordination Chemistry.

GREEN CHEMISTRY: PROPERTIES AND APPLICATIONS OF IONIC LIQUIDS

Douglas R. MacFarlane, Colin L. Raston, Janet L. Scott and Ching Mei Teoh
Department of Chemistry, Monash University, Clayton, Melbourne, 3800, Victoria; janet.scott@sci.monash.edu.au

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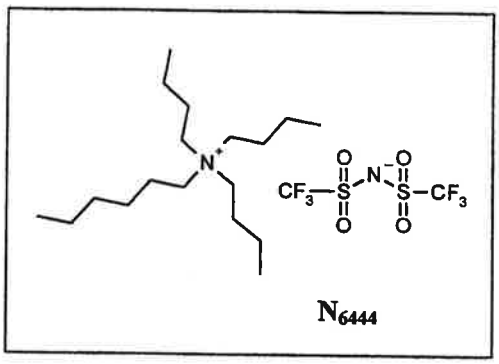
Salts with low symmetry cations, such as those recently prepared in our group[1], based on the quaternary ammonium ion and depicted here can have fusion temperatures below room temperature. These molten salts provide unique media for organic reactions.



N_{6444}

The negligible vapour pressure and relatively high stability of these salts, along with their ability to solubilise organic molecules make them attractive candidates for replacement of volatile or toxic organic solvents in synthetic procedures, at the same time diminishing the risk of fire or explosion.

We report the synthesis of a number of supramolecular host compounds, both known and novel, in high yield and purity using the molten salt (code-named N_{6444}) depicted above as the liquid reaction medium. The wide liquid range of the ionic liquid and its complete lack of volatile components leads to energy efficient, clean recycling of the reaction medium after separation of the product which requires only washing for purification.

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Reactions of Iminodiacetate Bound to Cobalt(III) as a Didentate Ligand.

OP 39

Richard M. Hartshorn

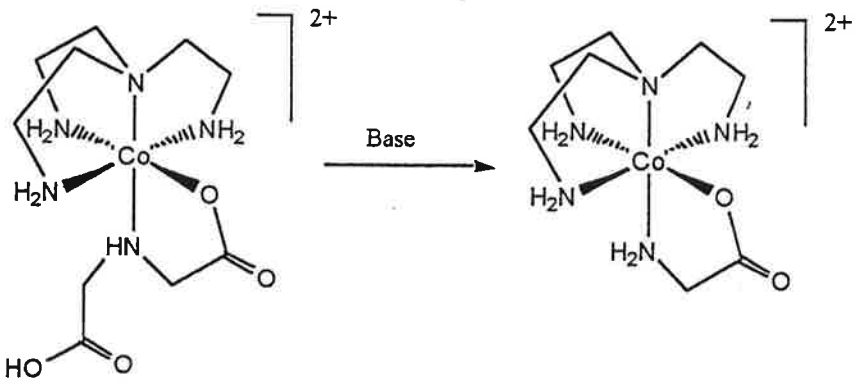
Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

r.hartshorn@chem.canterbury.ac.nz

Iminodiacetate (IDA^{2-}) is a potentially tridentate ligand, and there are many complexes described in the literature where it coordinates in this manner. This project was undertaken in order to explore the chemistry of complexes where this ligand, or an analogue, is bound as a didentate ligand.

The tetradentate ligand tris(2-aminoethyl)amine (tren) was chosen to occupy the remaining four coordination sites on the cobalt(III) ion as it should be a sufficiently good ligand to minimise substitution by a tridentate ligand. This tripodal ligand should also minimise the number of possible diastereoisomers, as it will be symmetrically disposed over the four coordination sites.

Treatment of the $IDAH^-$ complex with aqueous base gives rise to the *p*-$[Co(tren)(gly)]^{2+}$ ion, as shown below. This paper will describe the results from experiments that have been undertaken in order to identify possible mechanisms for this reaction.



The low yield and production of significant amounts of cobalt(II) during the reaction may imply a mechanism involving oxidation of the ligand at the expense of the metal ion. The results of crossover studies, employing bis(1,2-diaminoethane) complexes, and other experiments, are consistent with this proposal. Attempts have been made to establish whether it is the chelated or pendant portion of the $IDAH^-$ that gives rise to the glycine fragment.

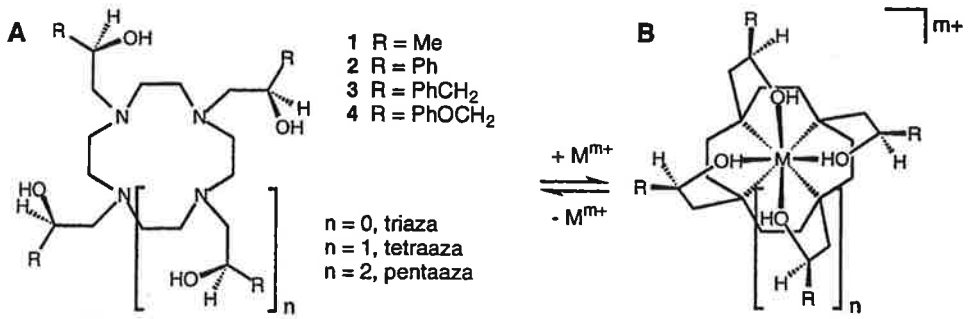
Aspects of Complexation and Supramolecular Chemistry in Metal Complexes of Pendant Arm Polyazamacrocycles

Mark A. Buntine,[a] Stephen F. Lincoln,[a*] Christopher B. Smith,[b] Ashley K. W. Stephens,[b] Kylie M. Tonkin,[b] Kia S. Wallwork,[b] Jennifer M. Weeks,[a] Oska Wyness,[a] and Kevin P. Wainwright[b*]

[a]*Department of Chemistry, University of Adelaide, Adelaide, SA 5005, Australia*

[b]*Department of Chemistry, The Flinders University of South Australia, Adelaide, GPO Box 2100, SA 5001, Australia*

The complexation of a selection of the pendant arm triaza-, tetraaza- and pentaazamacrocycles, **A**, by a range of metal ions produces a fascinating array of complexes, **B**, whose stabilities and labilities have been characterised. The chiral centres in each ligand are either all *R* or all *S* which results in each ligand and each metal complex being homochiral. It also produces a bowl-shaped molecular receptor site above the oxygen plane, the depth and diameter of which depends on the particular ligand. Several examples of molecular reception have been observed both in solution and the solid state.



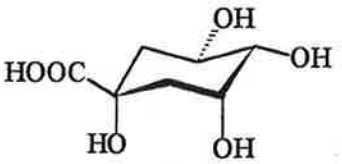
Potentiometric complexation, NMR kinetic, crystallographic and molecular modelling studies are discussed.

STABILIZATION OF CHROMIUM(V/IV) BY A NATURALLY OCCURRING LIGAND, QUINIC ACID

OP 41

Rachel Codd, Aviva Levina and Peter A. Lay
School of Chemistry, University of Sydney, Sydney 2006 NSW, Australia
E-mail: levina_a@chem.usyd.edu.au

Quinic acid (**I**, qaH_5) is widely distributed amongst higher plants,[1] where it is thought to act as a ligand and carrier of metal ions,[2] due to the presence of several attractive chelating sites (2-hydroxycarboxylato and 1,2-diolato moieties). Of particular interest to us was the potential ability of **I** to stabilize the "unusual" oxidation states, Cr(V) and Cr(IV), which are the likely reactive species in Cr(VI)-induced genotoxicities.[3]



I

A relatively stable complex **II**, $K[Cr^{V}O(qaH_3)_2]$, has been isolated in the solid state and characterized by a range of techniques, including XAFS spectroscopy.[4,5] This is the first isolated and fully characterized Cr(V) complex with a naturally occurring ligand. The linkage isomerism of **II** in aqueous solutions, involving 2-hydroxycarboxylato and 1,2-diolato moieties of **I**, has been investigated by EPR spectroscopy.[4] Reaction of Cr(VI) with **I** in methanol, used as a synthetic route to **II**, has been shown to pass through Cr(IV) intermediates.[5] Quantitative generation of a Cr(IV)–**I** complex in aqueous solution has been achieved by the reaction of Cr(VI) with As(III) in the presence of excess **I**,[6] and its solution structure **III**, $[Cr^{IV}O(qaH_4)_2]^0$, has been determined by XAFS spectroscopy. The complex **III** is probably the most stable one in neutral aqueous media among known Cr(IV) complexes.[6] The complexes **II** and **III** are able to induce oxidative DNA cleavage *in vitro*.[7] Implications of these results to the mechanisms of Cr(VI)-induced genotoxicities and carcinogenicities will be discussed.

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Carbon-Heteroatom Bond Activation on Ruthenium(0) Complexes

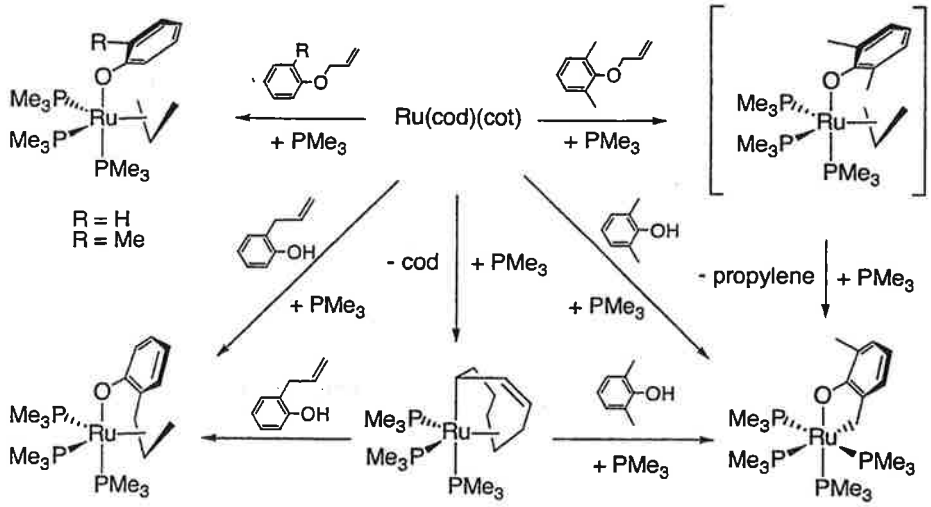
OP 42

Sanshiro Komiya
Department of Applied Chemistry, Tokyo University of Agriculture and Technology
2-24-16 Nakacho, Koganei, Tokyo 184-8588 Japan; Email: komiya@cc.tuat.ac.jp

Ruthenium-mediated organic chemical tranformations are one of the recent interests due to their high selectivity, specificity and efficiency. Although they frequently involve metal-assisted activation of carbon-heteroatom bonds, their mechanisms and controlling factors are not well understood in comparison with the well described chemistry of gorup 10 metals. We recently found that C-hetero atom bonds (R-Y) in alkenyl ethers, esters and sulfides smoothly are smoothly activated by Ru(cod)(cot) (1) (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) in the presennce of tertiary phosphine ligands to give oxidative addition products Ru(R)(Y)Ln and/or their coordination compounds. Coordination scheme of the cycloolefin ligands in **1** also varies very much depending on ligand employed and reaction conditions, controlling their chemical reactivity.

When **1** was treated with 2,6-dimethylphenyl allyl ether in the presence of PMe_3, C-H bond in ortho-Me substituent was metalated giving new ruthenacycle with liberation of propylene. 2,6-Dimethylphenol or 2-allylphenol also reacted with 1/PMe_3 to give ruthenacycles. Further carbonylation or reactions with acetylenes of these ruthenacycles lead to benzolactones or benzopyran derivatives. Novel structures and reactivities of these ruthenium complexes will be presented.

Scheme 2. Successive CO/CH or OH/CH Bond Activation



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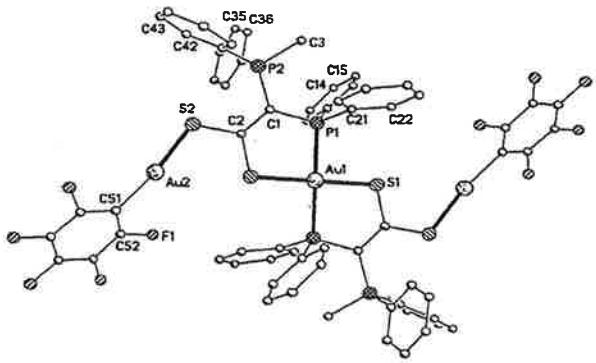
Sensors for VOC´s based on organogold thiolate complexes.

M. Laguna[a], C. Bariáin[b], J. Garrido[b], P. G. Jones[c], I.R. Matias[b] and. I. Romeo[b].

a) Instituto de Ciencia de Mariales de Aragón, Universidad de Zaragoza. Plaza S. Francisco 50009 Zaragoza Spain. E-mail mlaguna@posta.unizar.es
b) Departamento de Química Aplicada y Departamento de Ingeniería Eléctrica, U.P.Na, Campus de Arrosadia s/n, E-310006, Pamplona, Spain.
c) Institut für Aanorganische and Analitischem Chemie, Technische Universität , Braunschweig, Postfach 3329, D-38023, Braunschweig, Germany.

In 1995 Mann and co-workers showed that the double salts $[PtL_4][M(CN)]$ (L=arylisonitrile; M= Pt, Pd) were sensitive to the presence of volatile organic compounds (VOC´s). Recently Eisenberg and coworkers reported a similar behaviour for a dimeric gold(I) dithiocarbamate.

In this work we present organometalic gold(I) complexes that show a reversible vapochromic shift under exposure to VOC´s. The synthesis of this complexes was acomplished via addition of $[Au(tht)_2]X$ to a dichlorometane solution of $[Au(PPh_2C(CSSPPh_2Me)_2][Au(C_6F_5)_2]$ whose synthesis was described previously by us. The structure obtained by X-Ray difracction study is showed above.



We study the sorptive properties of this complexes towards some representative VOC´s by NMR technic and termogravimetric and BET surface isotherms analysis. Absorption vapochromic shift with diferent organic solvents were determined by UV-Vis light reflexion on solid samples. We also incorporate this dyes in a silica matrix made by the sol-gel process with was integrated in an optical fiber sensor device. Monitoring of VOC´s in the 100ppm range is possible with this design.

The Fluxionality of $[Fe_3(CO)_{12}]$ and its Derivatives

OP 44

by S.C.M. Agustinho, X. Chen, Brian E. Mann, and S. Smith

Department of Chemistry, The University of Sheffield, Sheffield, S3 7HF, England.
b.mann@sheffield.ac.uk

Although originally, the fluxionality of $[Fe_3(CO)_{12}]$ was originally described in terms of the merry-go-round mechanism,[1] it was shown in 1989 that this mechanism has a $\Delta G^{\ddagger}$ ~40 kJ mol^{-1}, and that a lower energy mechanism is present.[2] There are two descriptions of the lowest energy fluxionality of $[Fe_3(CO)_{12}]$. Johnson originally proposed a mechanism involving librations of of the Fe_3 triangle about the C_2 axis through the unbridged iron and the centre of the carbonyl bridged iron atoms.[3] Subsequently, it was proposed that the Fe_3 triangle rotates about an S_{10} axis of the carbonyl icosahedron.[4] This proposal was supported by Bürgi-Dunitz mapping of the dynamic pathway,[5] and a web movie.[6] The mechanism is still disputed.[7]

In order to provide further evidence, derivatives of the complexes $[Fe_3(CO)_{10}(Ph_2PEPPh_2)]$, E = CH_2, $(CH_2)_2$, $(CH_2)_4$, NH, and $[Fe_3(CO)_{10}\{(EtO)_2POP(OEt)_2\}]$ have been synthesised and investigated by X-ray crystallography, except $[Fe_3(CO)_{10}\{Ph_2P(CH_2)_4PPh_2\}]$, and NMR spectroscopy. In each case the, chelate ligand bridges an Fe_2 edge of the Fe_3 triangle.

The presence of the chelate ring in $[Fe_3(CO)_{10}(Ph_2PEPPh_2)]$, E = CH_2, NH, and $[Fe_3(CO)_{10}\{(EtO)_2POP(OEt)_2\}]$ results in substantial distortion of the molecule from the idealized C_{2v} structure of $[Fe_3(CO)_{12}]$, as predicted by rotation of the Fe_3 triangle about the S_{10} axis of the carbonyl icosahedron. The fluxionality of these compounds is also consistent with this pathway being the lowest energy one.

In $[Fe_3(CO)_{10}\{Ph_2P(CH_2)_2PPh_2\}]$, the $Fe_2P(CH_2)_2P$ part of the molecule adopts a chair conformation. The lowest energy pathway is the merry-go-round mechanism with inversion of the chair occurring at higher energy.

We wish to thank The Royal Society, Instituto de Quìmica de São Carlos - USP, FAPESP, Brazil, and the University of Sheffield for financial support.

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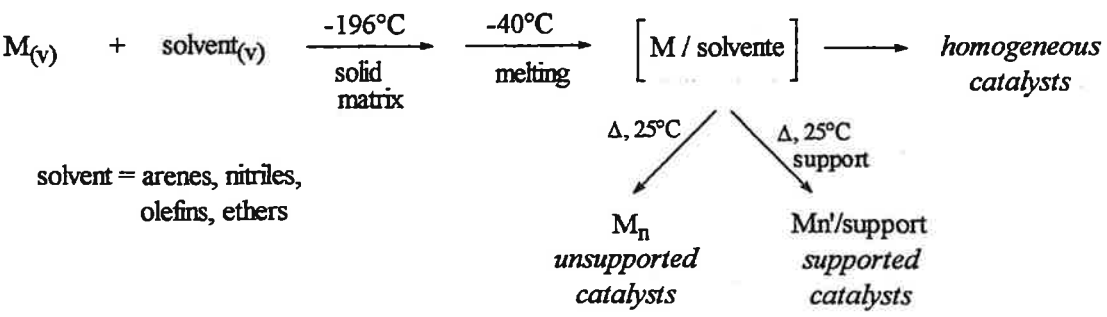
Advances in the Metal Vapour Derived Catalysts

OP 45

Giovanni Vitulli

Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa (Italy). E-mail: pervit@dcci.unipi.it

The metal vaporization provides an efficient route to nanostructured homo and heterometallic catalysts [1]. Metal vapour when deposited at low temperature into weakly complexing organic media (such as toluene, tetrahydrofurane, pentane or similar organics) can allow the formation of reaction product solutions stable at low temperature (solvated metal atoms). They contain solvent stabilized microclusters in which the interaction of the organic ligand with the metal is so weak that they can be regarded as naked metal clusters. Such solutions can be directly used as precursors for a wide range of homogeneous catalytic reactions; the warming up from the isolation temperature (-50°C ÷ -30°C) to room temperature results in a clustering process which affords nanostructured metal particles as powders or as supported metal aggregates (Scheme).



Scheme

The method ensures the generation of small metal particles in their reduced state and no activation steps are necessary. Choice of the ligand can be rightly overseen in order to exert a valuable control over metal cluster sizes.

By mixing different solvated metal atoms or by simultaneous vaporization of two metals, the technique can be conveniently employed to prepare intermetallic aggregates.

Examples of unusual catalytic reaction promoted by metal vapour derived catalysts will be presented.

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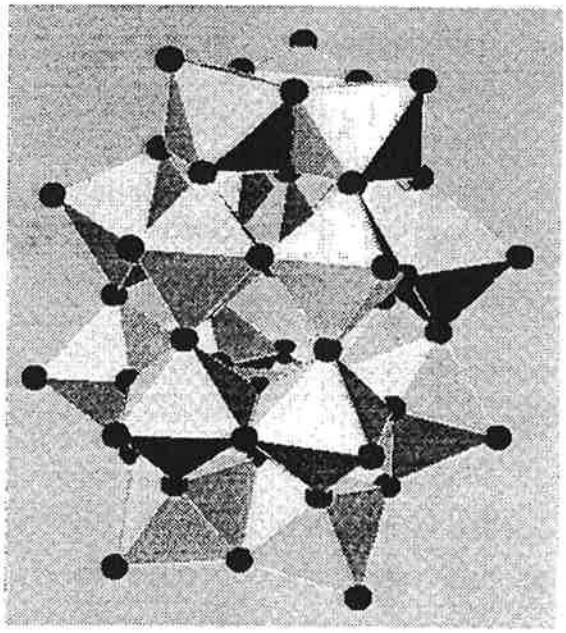
The New Classic Heteropoly Anion, $[S_2W_{18}O_{62}]^{4-}$ **OP 46**

Peter J. S. Richardt, Alan M. Bond† and Anthony G. Wedd

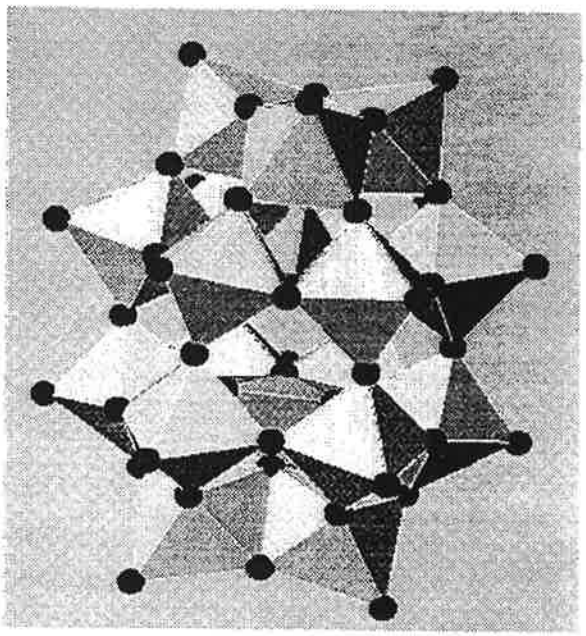
School of Chemistry, University of Melbourne, Parkville, 3052.
†Department of Chemistry, Monash University, Clayton, 3168.
(t.wedd@chemistry.unimelb.edu.au)

The hetero-atom X in polyoxoanion clusters, $[X_xM_yO_z]^{n-}$, determines the anionic charge. For example, X = Si^{IV}, P^V or S^{VI} in the tungsten(VI) Dawson anions $[X_2W_{18}O_{62}]^{n-}$ leads to n = 8, 6 or 4, respectively. The progressive decrease in anionic charge leads to positive shifts in reduction potentials allowing redox activity to be photo-induced. This aspect has been explored recently in the $[S_2Mo_{18}O_{62}]^{4-}$ system.[1,2]

A new heteropolyoxotungstate $[S_2W_{18}O_{62}]^{4-}$ has been isolated and structurally defined. While it is a Dawson anion, its Bu_4N^+ salt contains the second only example of a γ^* isomer (D_{3d} point symmetry), rather than the common α form (D_{3h}). The consequences of this structural variation and a spectacular redox chemistry will be described.



α isomer (D_{3h})



γ^* isomer (D_{3d})

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Porous, Chiral Molecular Framework Materials - Crystal and Guest-Exchange Chemistry

Cameron J. Kepert,[§] Timothy J. Prior, Matthew J. Rosseinsky

[§] School of Chemistry, University of Sydney, NSW 2006, Australia

c.kepert@chem.usyd.edu.au

The exploration of extended lattices of interconnected molecular species, or molecular framework materials, is providing significant advancements in rational materials design. Recent reports have demonstrated microporosity in these materials, as seen in their ability to support void micropore volume, to display high degrees of selectivity and reversibility in their desorption/sorption chemistry, and to possess catalytic activity. These breakthroughs have drawn a direct link with well-known microporous materials such as zeolites and have led to suggestions that molecular framework materials have potential for application in separations, sensing and heterogeneous catalysis.

One area where conventional microporous materials have made comparatively little impact is enantioselective sorption and catalysis due to the difficulty in preparing chiral structures without enantiomer intergrowth and with void volume accessible by template removal or exchange. Recent developments in the construction of molecular framework materials has seen significant advances in this area with the discovery of some of the only porous, chiral materials known. Here we present two extensive families of crystalline coordination framework, members of which provide the majority of all porous, chiral inorganic materials yet discovered. The chirality of these materials originates from the presence of extended three-fold coordination frameworks based on the (10,3)-a network, both phases having unique network topologies and space group symmetries. The first of these phases contains interconnected 13 Å microcavities and 28% pore volume, and the second contains 16 Å microchannels and 51% pore volume. The second phase may be synthesised homochirally due to a unique chiral templating effect. Both phases display reversibility and selectivity in their sorption chemistry, as seen following guest-desorption and through in-situ characterisations of guest-exchange.

$Ca_7Nb_6Zr_7O_{36}$ - SYNTHESIS AND STRUCTURE REFINEMENT OF A NEW ANION-DEFICIENT, FLUORITE-RELATED SUPERSTRUCTURE PHASE

Siegbert Schmid

Wood Science Laboratory, Department of Forestry, Australian National University, Canberra ACT 0200, Australia

An attempt to systematically investigate the $CaZrO_3$ - $LiTaO_3$ system has led to the discovery of a new long period anion-deficient, fluorite-related superstructure phase with composition $Ca_7Ta_6Zr_7O_{36}$ [1]. Electron diffraction suggested a space group symmetry for this phase of *Fddd,* and a relationship to the so-called cubic stabilised zirconias (CSZs) and other fluorite-related superstructure phases such as $CaZr_4O_9$ which also show additional scattering in similar regions of reciprocal space. The refined metal ordering is far from fully ordered, and is reminiscent of the A/B ordering characteristic of the pyrochlore structure type [2].

It proved possible to grow very small single crystals of the related superstructure phase $Ca_7Nb_6Zr_7O_{36}$ and a full sphere of intensity data was collected at the vertical wiggler beamline BL-14A of the Photon Factory, Tsukuba, Japan at $\lambda = 0.75$Å. The results of structure solution and refinement will be compared to the previous structure. The apparent structural flexibility may well manifest itself in interesting, technologically useful properties.

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Confinement of $[(H_2O)_2 \cap (18\text{-Crown-6})]$ in a Disc Shaped Cavity Lined with Six Nickel(II) Macrocycle Dimers

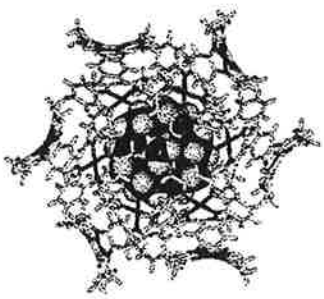
OP 49

Peter J. Nichols and Colin L. Raston

Department of Chemistry, Monash University, Clayton, Melbourne, Victoria 3800 Australia

Ni(TMTAA), [5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine-nickel(II)], is a versatile receptor for a range of globular like molecules.[1-3] Ni(TMTAA) acts as a divergent receptor with C_{60} in a 1:1 complex where there is a fullerene perched in each cavity of the macrocycle in an infinite zigzag array.[1] For smaller globular molecules 1,2-dicarbadodecaborane(12), phosphorus sulfide , phosphorus selenide and sulfur , Ni(TMTAA) self associates through aromatic faces into dimers. These dimers then act as divergent homotopic receptors, the complexes having a 1:2 ratio of guest to host species.[1,2] Ni(TMTAA) can also form inclusion complexes with the solvent toluene and has been found to have at least three different structures in its unsolvated form.[2,4,5] In some of these structures the metal macrocycle self associates through the methyl-lined faces into dimers.[2] Complementarity of size and curvature of the interacting components seems to be a prime determinant of the supramolecular outcomes.

We now report new findings on the host - guest chemistry of the Ni(TMTAA) whereby there is an extended self association of the divergent receptors around a large disc-shaped cavity. The cavity has been found to contain CS_2 molecules (disordered in the determine structure) or an 18-crown-6 molecule, associated via hydrogen bonding to two water molecules, which fits snugly into the void and is symmetry matched to the Ni(TMTAA) assembly.



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LIST OF DELEGATES

Surname	Given Names	Address	Phone	Email Address	Presentation(s)
Aldrich-Wright	Janice	Department of Chemistry University of Western Sydney MACARTHUR NSW 2560 AUSTRALIA	02 4620 3218	J.Aldrich-Wright@uws.edu.au	**PT68**
Ammala	Paul	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4535	paul.ammala@sci.monash.edu.au	**OP8**
Anderberg	Pia	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 6565	panderbe@chem.usyd.edu.au	**PT43**
Andrews	Phil	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4514	p.andrews@sci.monash.edu.au	**OP24, PM5, PM6**
Angus	Patricia	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 0504	pma@rsc.anu.edu.au	
Anwar Amin	Ahmed	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4425	anwar-a@chem.usyd.edu.au	**PT40**

Appleton	Trevor	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 4005	appleton@chemistry.uq.edu.au	PM36, PM37
Armstrong	Robert	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 3104	R.Armstrong@chem.usyd.edu.au	**OP5**
Arnold	Dennis	School of Physical Sciences Queensland University of Technology BRISBANE QLD 4001 AUSTRALIA	07 3864 2482	d.arnold@qut.edu.au	PM22
Ayoko	Godwin	Centre for Medical and Health Physics Queensland University of Technology BRISBANE QLD 4001 AUSTRALIA	07 3864 5232	g.ayoko@qut.edu.au	**PM20, PM21**
Baker	Anthony	Department of Chemistry, Materials and Forensic Science University of Technology Sydney PO Box 123 Broadway SYDNEY NSW 2007 AUSTRALIA	02 9514 1764	tony.baker@uts.edu.au	**PT63, PT64, PT65**
Baker	Murray	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9380 2576	mvb@chem.uwa.edu.au	**OP6, PM48,** PM49, PM50

Barnard	Peter	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 7600	barnardp@chem.usyd.edu.au	**PT33**
Battle	Andrew	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4270	battle_a@alf.chem.usyd.edu.au	**PT29**
Bayler	Angela	School of Chemistry University of Tasmania HOBART TAS 7001 AUSTRALIA	03 6226 2158	angela.bayler@utas.edu.au	**PM56**
Bennett	Martin	Research School of Chemistry, Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 3639	bennett@rsc.anu.edu.au	**PL6**, PM60, PM63, PM64, PM65
Berben	Louise	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 5473	louiseberben@hotmail.com	**PT55**
Bernardo	Martha	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4334	marthab@rsc.anu.edu.au	**PM81, PM85**
Bernhardt	Paul	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 4266	bernhardt@chemistry.uq.edu.au	PM38, PM39, **PM40**, PM41, PM42, PM43, PM46

Best	Stephen	School of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 6505	s.best@chemistry.unimelb.edu.au	**K8**, PT10, PT11, PT12, PT13
Bhargava	Suresh	Department of Applied Chemistry RMIT University GPO Box 2476V MELBOURNE VIC 3000 AUSTRALIA	03 9925 3365	suresh.bhargava@rmit.edu.au	PM60, PM61
Bond	Alan	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 1338	a.bond@sci.monash.edu.au	PM1
Bondin	Mark	School of Chemistry University of Melbourne PARKVILLE MELBOURNE VIC 3052 AUSTRALIA	03 9344 7015	m.bondin@ugrad.unimelb.edu.au	**PT13**
Borg	Stacey	School of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 7015	s.borg@chemistry.unimelb.edu.au	**PT12**
Bosnich	Brice	Department of Chemistry University of Chicago 5735 South Ellis Ave CHICAGO IL 60637 USA	+1 773 702 0287	bos5@midway.uchicago.edu	**OP27**

Bowman	Gary	Department of Chemistry University of Western Sydney Macarthur PO Box 555 CAMPBELLTOWN NSW 2560 AUSTRALIA	02 9820 5738	g.bowman@uws.edu.au	**PT69**
Bown	Mark	CSIRO Molecular Science Bag 10 CLAYTON SOUTH VIC 3169 AUSTRALIA	03 9545 2501	Mark.Bown@molsci.csiro.au	
Boyd	Peter	Department of Chemistry University of Auckland Private Bag 92019 AUCKLAND NEW ZEALAND	+ 64 9 373 7599	cheboyd@ccu1.auckland.ac.nz	**PM76, PM77**
Brasch	Nicola	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6279 9696	nbrasch@rsc.anu.edu.au	PM66, PM67
Brayshaw	Simon	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9330 2786	brayshaw@chem.uwa.edu.au	**PM50**
Brothers	Penelope	Department of Chemistry University of Auckland Private Bag 92019 AUCKLAND NEW ZEALAND	+64 9 373 7599	p.brothers@auckland.ac.nz	**OP25**

Brown	David	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9380 2576	dhbrown@chem.uwa.edu.au	**PM49**
Bruce	Michael	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 5939	michael.bruce@adelaide.edu.au	**OP15**, PT19
Burling	Suzanne	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 5745	s.burling@chem.usyd.edu.au	**PT41**
Byrnes	Matthew	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 3641	byrnes@rsc.anu.edu.au	**OP10**
Caiazza	Daniela	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 4837	dcaiazza@chemistry.adelaide.edu.au	**PT21**
Canty	Allan	School of Chemistry University of Tasmania HOBART TAS 7001 AUSTRALIA	03 6226 2162	allan.canty@utas.edu.au	PM56, PM57
Chatterjee	Swarup	Department of Chemistry Australian National University CANBERRRA ACT 0200 AUSTRALIA	02 6249 3159	swarup.chatterjee@anu.edu.au	**PM75**

Cifuentes	Marie	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4293	marie.cifuentes@anu.edu.au	**PM70**, PM71, PM72
Colbran	Stephen	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 938 4737	s.colbran@unsw.edu.au	**OP23**, PT55, PT56, PT57, PT58, PT59
Cregan	Andrew	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 3715	cregan@rsc.anu.edu.au	**PM67**
Cross	Maddalena	School of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 6491	m.lucarelli@pgrad.unimelb.edu.au	**OP9**
D'Alessandro	Deanna	Department of Chemistry James Cook University TOWNSVILLE QLD 4811 AUSTRALIA	07 4727 7262	Deanna.Dalessandro@jcu.edu.au	
Dance	Ian	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 4703	I.DANCE@unsw.edu.au	PT46, PT47, PT48, PT49, PT50, PT51
Davies	Murray	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4270	m.davies@chem.usyd.edu.au	**PT26, PT27**

De Iuliis	Geoffry	Department of Chemistry University of Newcastle CALLAGHAN NSW 2308 AUSTRALIA	02 4921 8965	cpgd@paracelsus.newcastle.edu.au	**PM23**
Delfs	Christopher	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 3017	christopher.delfs@anu.edu.au	PM78, **PM79, PM80**
Diakos	Connie	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 3125	c.diakos@chem.usyd.edu.au	**PT25**
Dickson	Ron	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4560	ron.dickson@sci.monash.edu.au	**OP14, PM10,** PM11
Dong	Ying	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4852	y.dong@chem.usyd.edu.au	**PT35**
Donnelly	Paul	Department of Chemistry University of Western Australia NEDLANDS WA 6009 AUSTRALIA	08 9380 3170	pdonnell@chem.uwa.edu.au	**PM54**
Doonan	Christian	School of Chemistry University of Melbourne MELBOURNE VIC 3010 AUSTRALIA	03 9344 6473	c.doonan@student.unimelb.edu.au	PT6, **PT7**

Driver	Jenni	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4380	jdriver@cfmeu.asn.au	**PM78**
El-Khateeb	Mahmoud	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 3527	m.khateeb@chemistry.uq.edu.au	**PM37**
Evans	Andrew	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 5473	Andrewe@student.unsw.edu.au	**PT56**
Evans	Cameron	Department of Chemistry University of Waikato PO Box 3105 HAMILTON NEW ZEALAND	+64 7 8384219	ce1@waikato.ac.nz	**PM68**
Fackler	John	Texas A&M University College Station TX 77843-3012 USA	+1 409 845 0648	Fackler@mail.chem.tamu.edu	**K6**
Fainerman–Melnikova	Marina	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 3125	M.Fainerman@chem.usyd.edu.au	**PT32**
Fisher	Keith	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 4673	k.fisher@unsw.edu.au	**OP37, PT52**

Flanagan	Bernadine	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 4600	B.Flanagan@chemistry.uq.edu.au	**PM41**
Freeman	Hans	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4405	freemanh@chem.usyd.edu.au	
Friedrich	Holger	Department of Chemistry University of Natal DURBAN 4041 SOUTH AFRICA	+27 31 2603107	friedic@scifs1.und.ac.za	**PT71**
Funston	Alison	School of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 4125	a.funston@chemistry.unimelb.edu.au	**PT3**
Gahan	Lawrence	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 3844	gahan@chemistr y.uq.edu.au	PM35, PM37
Gardiner	Michael	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 6351 2297	M.Gardiner@chem.usyd.edu.au	**OP16, PT44**
Geue	Jason	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 4570	jgeue@chemistry.adelaide.edu.au	**OP20**

Gitlits	Alex	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4576	agitlits@vaxc.cc.monash.edu.au, agitlits@hotmail.com	**PM15, PM16**
Goh	Lai Yoong	Department of Chemistry National University of Singapore Lower Kent Ridge Rd SINGAPORE 119260	+65 874 2677	chmgohly@nus.edu.sg	**OP32**
Griffith	Christopher	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9380 1823	cgriff@chem.uwa.edu.au	**PM47**
Griffith	William	Department of Chemistry Imperial College of Science Technology and Medicine LONDON SW7 2AY UK	+44 171 594 5759	w.griffith@ic.ac.uk	**OP31**
Grubbs	Robert	Division of Chemistry and Chemical Engineering, 164-30 California Institute of Technology PASADENA, CA 91125 USA	+1 626 395 6003	rhg@its.caltech.edu	**PL3**
Guan	Peisen	School of Chemistry University College (UNSW) Australian Defence Force Academy CANBERRA ACT 2601 AUSTRALIA	02 6268 8917	p-guan@adfa.edu.au	
Habermehl	Nicolle	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4334	nicolle@rsc.anu.edu.au	**PM82**

Hahn	Thilo	Department of Inorganic Chemistry University of Leipzig Johannisallee 29 D-04103 LEIPZIG GERMANY	+49 341 9736 151	hey9@server1.rz.uni-leipzig.de	**PM34**
Hall	Matthew	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4270	hall_m@chem.usyd.edu.au	**PT27, PT28**
Hambley	Trevor	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 2830	t.hambley@chem.usyd.edu.au	**OP21,** PM17, PT25, PT26, PT27, PT28, PT29, **PT30, PT31,** PT38
Hamilton	Ian	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4334	ianh@rsc.anu.edu.au	**PM83**
Hardie	Michaele	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4598	m.hardie@sci.monash.edu.au	**OP4,** PM8, **PM9**
Harper	Joanne	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 3641	joanne@rsc.anu.edu.au	**PM64**
Hartshorn	Richard	Department of Chemistry University of Canterbury Private Bag 4800 CHRISTCHURCH NEW ZEALAND	+64 3364 2874	r.hartshorn@chem.canterbury.ac.nz	**OP39**

Haupt	Rebecca	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6267 5328	rebecca@rsc.anu.edu.au	PM66
Hauser	Andreas	Département de chimie physique Université de Genève 30 quai Ernest-Ansermet 1211 GENEVA SWITZERLAND		andreas.hauser@chiphy.unige.ch	**PL2**
Hayes	Elizabeth	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 3527	E.Hayes@chemistry.uq.edu.au	**PM42**
He	Zhicong	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9785 5473	z.he@unsw.edu.au	**PT58**
Heath	Graham	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4039	heath@rsc.anu.edu.au	PM70
Heck	Jürgen	Institut für Anorganische und Angewandte Chemie Universität Hamburg Martin-Luther-King-Platz 6 D-20146 HAMBURG GERMANY	+49 40 42838 6375	heck@chemie.uni-hamburg.de	**PL1**
Helmstedt	Ulrike	Department of Chemistry James Cook University TOWNSVILLE QLD 4811 AUSTRALIA	07 4781 4750	Ulrikehelmstedt@unicum.de	**PM32**

Hill	Lyndal	University of Melbourne Masson Rd MELBOURNE VIC 3052 AUSTRALIA	03 9344 6491		
Hoang	Huy	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 3527	s336191@student.uq.edu.au	**PM36**
Hodgson	Margaret	Centre for Instrumental and Developmental Chemistry QUT GPO Box 2434 BRISBANE QLD 4001 AUSTRALIA	07 3864 5243	m.hodgson@qut.edu.au	**PM22**
Horn	Caitlin	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 4668	caitlin@student.unsw.edu.au	**PT49**
Humphrey	Mark	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 2927	mark.humphrey@anu.edu.au	PM70, PM71, PM72, PM73, PM80
Hurst	Steph	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4240	ralph.hurst@anu.edu.au	**PM73**

Jackson	Greg	School of Chemistry University College (UNSW) Australian Defence Force Academy CANBERRA ACT 2600 AUSTRALIA	02 6268 8679	wgj@adfa.edu.au	PT15, PT16, PT17
Jee	Bettina	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA		bettina.jee@student.unsw.edu.au	
Jensen	Paul	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4513		PM13, **PM14**
Ji	Xue-Kui	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4852	ji_x@alf.chem.usyd.edu.au	**PT39**
Junk	Peter	Department of Chemistry James Cook University TOWNSVILLE QLD 4811 AUSTRALIA	07 4781 4523	peter.junk@jcu.edu.au	PM27, PM28, PM29, **PM30, PM31**, PM32
Keene	Richard	School of Biomedical & Molecular Sciences James Cook University TOWNSVILLE QLD 4811 AUSTRALIA	07 4781 4343	Richard.Keene@jcu.edu.au	**OP7**, PM33

Kennedy	Brendan	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 2742	b.kennedy@chem.usyd.edu.au	**PT30**, PT31
Kepert	Cameron	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 5741	c.kepert@chem.usyd.edu.au	**OP47, PT72, PT73**
Komiya	Sanshiro	Department of Applied Chemistry Tokyo University of Agriculture and Technology 2-24-16 Nakacho Koganei TOKYO 184-8588 JAPAN	+81 423 88 7043	komiya@cc.tuat.ac.jp	**OP42**
Kopp	Mike	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 3508	kopp@rsc.anu.edu.au	**PM65**
Koutsantonis	George	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9380 3177	gak@chem.uwa.edu.au	PM47
Laguna	Mariano	Instituto Ciencia de Mariales de Aragon Universidad de Zaragoza Plaza S. Francisco 50009 ZARAGOZA SPAIN	+34 976 761181	mlaguna@posta.unizar.es	**OP43**

Lau	Connie	School of Chemistry Australian Defence Force Academy CANBERRA ACT 2600 AUSTRALIA	02 6268 8943	c-lau@adfa.edu.au	
Lawrance	Geoffrey	Department of Chemistry University of Newcastle CALLAGHAN NSW 2308 AUSTRALIA	02 4921 5474	csgl@paracelsus.newcastle.edu.au	PM23, PM24, PM25, PM26
Lay	Peter	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4269	lay_p@chem.usyd.edu.au	**K10, PT30**, PT31, PT32, PT33, PT34
Leary	Stuart	Department of Chemistry James Cook University TOWNSVILLE QLD 4811 AUSTRALIA	07 4781 4283	sci-sgl@jcu.edu.au	**PM32**
Levina	Aviva	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 7600	levina_a@chem.usyd.edu.au	**OP41, PT34**
Lewin	Mark	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9622 5828	z2192343@student.unsw.edu.au	**PT48**
Lewis	Gareth	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 4707	gareth.lewis@unsw.edu.au	**OP3**, PT46, PT47

Lim	Kevin	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9443 2773	kevin@crystal.uwa.edu.au	**PM52**
Lincoln	Stephen	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 5559	stephen.lincoln@adelaide.edu.au	**OP40**
Lindoy	Leonard	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4400	l.lindoy@chem.usyd.edu.au	PT35, PT36, PT37, PT38, PT39
Lonnon	David	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 5473	D.Lonnon@student.unsw.edu.au	PT58, **PT59**
Lorenzo	Susan	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	03 9385 4726	s.lorenzo@student.unsw.edu.au	**PT47**
Louis	Lance	Department of Chemistry James Cook University TOWNSVILLE QLD 4811 AUSTRALIA		Lance.Louis@jcu.edu.au	**PM29, PM30**
Lu	Max G.Q.	Chemical Engineering Department University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 3735	maxlu@cheque.uq.edu.au	

Lucas	Nigel	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4230	nigel.lucas@anu.edu.au	**PM71**
Lüthi	Stefan	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 4107	luethi@chemistry.uq.edu.au	**OP1, PM44,** PM45
Macpherson	Brendan	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 4600	B.Macpherson@chemistry.uq.edu.au	**PM43**
Magnusson	Eric	School of Chemistry Australian Defence Force Academy CANBERRA ACT 2601 AUSTRALIA	02 6268 8298	eam@adfa.edu.au	
Maitlis	Peter	Department of Chemistry University of Sheffield Sheffield S3 7HF UK	+44 114 266 0888	P.Maitlis@Sheffield.ac.uk	**PL7**
Malarek	Michael	School of Chemistry University of Melbourne MELBOURNE VIC 3010 AUSTRALIA	03 9344 6473		**PT8**
Mann	Brian	Department of Chemistry University of Sheffield SHEFFIELD S3 7HF UK	+44 114 222 9332	b.mann@sheffield.ac.uk	**OP44**

Martin	Lisandra	Department of Chemistry Flinders University GPO Box 2100 ADELAIDE SA 5001 AUSTRALIA	08 8201 2465	Lisa.Martin@flinders.edu.au	**PT67**
Mashima	Kazushi	Department of Chemistry Graduate School of Engineering Science Osaka University Toyonaka OSAKA 560-8531 JAPAN	+81 6 6850 6247	mashima@chem.es.osaka-u.ac.jp	**OP33**
Mason	Dayna	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4576	dayna.mason@sci.monash.edu.au	**PM17**
Masters	Vanessa	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 4107	V.Masters@chemistry.uq.edu.au	**PM46**
Mathey	Francois	Laboratoire "Hétéroéléments et Coordination" UMR 7653 CNRS DCPH Ecole Polytechnique 91128 PALAISEAU cedex FRANCE	+33 1 6933 4079	francois.mathey@polytechnique.fr	**PL8**
Mays	Martin	Department of Chemistry University of Cambridge Lensfield Road CAMBRIDGE CB2 1EW UNITED KINGDOM	+44 1223 336324	mjm14@cam.ac.uk	**OP34**

McAllister	Duncan	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA		d.mcallister@chemistry.uq.edu.au	**PM45**
McCool	Brian	Department of Chemistry James Cook University TOWNSVILLE QLD 4811 AUSTRALIA	07 4781 4513	brian.mccool@jcu.edu.au	**PM28**
McFadyen	David	School of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 4222	d.mcfadyen@chemistry.unimelb.edu.au	PT2, PT3, **PT4, PT5**
McKenzie	Christine	Department of Chemistry University of Southern Denmark Campusvej55 DK-5230 ODENSE M DENMARK	+45 6550 2518	chk@chem.sdu.dk	**PT45**
McMurtrie	John	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9518 9306	j.mcmurtrie@student.unsw.edu.au	**PT46**
Messerle	Barbara	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 465	b.messerle@unsw.edu.au	**OP11**, PT25, PT41, PT53
Micallef	Leanne	School of Science Griffith University Nathan Campus BRISBANE QLD 4111 AUSTRALIA	07 3875 7728	l.micallef@mailbox.gu.edu.au	**PT60**

Millar	Andrew	School of Chemistry University of Melbourne MELBOURNE VIC 3052 AUSTRALIA	03 9344 6473	a.millar@pgrad.unimelb.edu.au	**PT6**
Mocerino	Mauro	School of Applied Chemistry Curtin University of Technology GPO Box U 1987 PERTH WA 6845 AUSTRALIA	08 9266 3125	m.mocerino@info.curtin.edu.au	**PM59, PT70**
Mohr	Fabian	Department of Applied Chemistry RMIT University GPO Box 2476V MELBOURNE VIC 3000 AUSTRALIA	03 9925 2128	s9409865@bunyip.ph.rmit.edu.au, fab_mohr@hotmail.com	**PM60, PM61**
Moore	Evan-Guy	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA		E.Moore@chemistry.uq.edu.au	**PM38, PM39**
Morgan	Ying	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4412	Morgan_Y@alf.chem.usyd.edu.au	**PT31**
Morizzi	Julia	Department of Applied Chemistry RMIT University GPO Box 2476V MELBOURNE VIC 3000 AUSTRALIA	03 9741 8339	s9305076@bunyip.ph.rmit.edu.au	**PM62**

Munk	Vivienne	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 2135	v.munk@chem.usyd.edu.au	**OP18**
Murray	Keith	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4512	Keith.S.Murray@sci.monash.edu.au	**K1**, PM3, PM12, PM13, PM14, PM28
Nakamura	Akira	Department of Chemistry Toho University 2-2-1 Miyama Funabashi CHIBA 274-8510 JAPAN	+81 6 6996 9462	anaka@chem.sci.osaka-u.ac.jp	**OP28**
Ness	Tim	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 1453	t.ness@sci.monash.edu.au	**PM4**
Newby	Leonora	School of Science Griffith University Nathan Campus BRISBANE QLD 4111 AUSTRALIA	07 3875 7728	l.newby@sct.gu.edu.au	**PT61**
Nichols	Peter	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4598	p.nichols@sci.monash.edu.au	**OP49**

Nicholson	Brian	Department of Chemistry University of Waikato Private Bag 3105 HAMILTON NEW ZEALAND	+64 78 562 889	b.nicholson@waikato.ac.nz	**PM68, PM69**
Nolan	Meredith	School of Science Griffith University Nathan Campus BRISBANE QLD 4111 AUSTRALIA	07 3875 7728	m.nolan@mailbox.gu.edu.au	**PT62**
Oats	Susan	School of Chemistry University of Tasmania GPO Box 252-75 HOBART TAS 7001 AUSTRALIA	03 6226 2158	Susan.Oats@utas.edu.au	**PM58**
Oliver	Pamela	Plenty Valley Christian School 17 Connor Street Bacchusmarsh MELBOURNE VIC 3340 AUSTRALIA	03 5367 3764		
Oyetunji	Olayinka	Department of Chemistry University of Botswana Private Bag UB 00704 GABORONE BOTSWANA		oyetunji@mopipi.ub.bw	**PT24**
Pace	Ron	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4546	Ron.pace@anu.edu.au	**K2**

Patel	Jim	School of Chemistry University of Tasmania GPO Box 252-75 HOBART TAS 7001 AUSTRALIA	03 6226 2158	j_patel@postoffice.utas.edu.au	**PM57**
Patterson	Brad	School of Biomedical and Molecular Sciences James Cook University TOWNSVILLE QLD 4811 AUSTRALIA	07 4781 7251	Bradley.Patterson@jcu.edu.au	**OP19, PM33**
Perkins	David	School of Chemistry University of Sydney SYDNEY NSW 2204 AUSTRALIA	02 9559 1617	d.perkins@alf.chem.usyd.edu.au	**PT36**
Pertici	Paolo	Department of Chemistry and Industrial Chemistry Italian National Council of Research University Of Pisa PISA 56126 ITALY	39 050 918224	pervit@dcci.unipi.it	**OP35**
Pfaltz	Andreas	Department of Chemistry University of Basel St. Johanns-Ring 19 CH-4056 BASEL SWITZERLAND	+41 61 267 1108	Andreas.Pfaltz@unibas.ch	**PL4**
Porter	Keith	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4334	porter@rsc.anu.edu.au	**PM86**

Powell	Clem	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4230	clem.powell@anu.edu.au	**PM72**
Price	David	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4577	David.Price@sci.monash.edu.au	**PM13**
Price	Jason	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4852	price_j@chem.usyd.edu.au	PT37
Priver	Steven	Department of Applied Chemistry RMIT University GPO Box 2476V MELBOURNE VIC 3000 AUSTRALIA	03 9925 2128	s9405510@bunyip.ph.rmit.edu.au	**PM61**
Rahman	Mokhlesur	Department of Chemistry University College (UNSW) Australian Defence Force Academy CANBERRA ACT 2600 AUSTRALIA	02 6268 8950	m-rahman@adfa.edu.au	**PT17**
Raine	Alan	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA		alanraine@hotmail.com	

Raston	Colin	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4577	c.raston@sci.monash.edu.au	**K3**, PM4, PM5, PM6, PM7, PM8, PM9, PM19
Raymond	Matthew	Department of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 7015	m.raymond@pgrad.unimelb.edu.au	**PT11**
Reed	Christopher	Department of Chemistry University of California Riverside RIVERSIDE CA 92521-0403 USA	+1 909 787 5197	chris.reed@ucr.edu	**K11**
Reger	Daniel	Department of Chemistry and Biochemistry University of South Carolina COLUMBIA SOUTH CAROLINA 29208 USA	+1 803 777 2587	Reger@psc.sc.edu	**OP36**
Rendina	Louis	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 4269	lou.rendina@adelaide.edu.au	**OP13**, PT21, PT22, PT23
Robins	Jason	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 1453	Jason.Robins@sci.monash.edu.au	**PM7**
Robinson	Brian	Department of Chemistry University of Otago PO Box 56 DUNEDIN NEW ZEALAND	+64 34 797 907	brobinson@alkali.otago.ac.nz	**OP26**

Roper	Warren	Department of Chemistry University of Auckland Private Bag 92019 AUCKLAND NEW ZEALAND	+64 9 373 7599	w.roper@auckland.ac.nz	**OP29**
Russell	Vanessa	Department of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 4668	v.russell@student.unsw.edu.au	**PT50**
Salem	Geoffrey	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4287	Geoff.Salem@anu.edu.au	**PM74**, PM75
Schiesser	Carl	School of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 4180	c.schiesser@chemistry.unimelb.edu.au	**K5**
Schmid	Siegbert	Department of Forestry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 2647	schmid@rsc.anu.edu.au	**OP48**
Scott	Janet	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 1338	janet.scott@sci.monash.edu.au	**OP38**
Scudder	Marcia	Department of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 4750	m.scudder@unsw.edu.au	PT46, **PT51**

Sharrad	Clint	Department of Chemistry University of Queensland BRISBANE QLD 4072 AUSTRALIA	07 3365 3882	c.sharrad@chemistry.uq.edu.au	**PM35**
Shaw	Aron	Department of Chemistry University of Newcastle CALLAGHAN NSW 2308 AUSTRALIA	02 4921 8965	cpas@paracelsus.newcastle.edu.au	**PM26**
Shaw	Warren	Department of Chemistry University of Sydney Building F11 SYDNEY NSW 2006 AUSTRALIA	02 9712 1218	Warren_s@chem.usyd.edu.au	**PT42**
Skelton	Brian	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9380 7107	bws@crystal.uwa.edu.au	PM15, PM16, PM29, PM47, PM48, PM49, **PM51**, PM52, PM53, PM54, PM56, PM57, PT19, PT37, PT39
Smith	Jonathan	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4577	jpsmith@its-sci1.cc.monash.edu.au	**PM12** PM3
Smith	Mark	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 5712	m1smith@chemistry.adelaide.edu.au	**PT19**

Smith	Matthew	Department of Chemistry James Cook University TOWNSVILLE QLD 4811 AUSTRALIA	07 4781 4750	Matthew.Smith@jcu.edu.au	**PM27**
Smyth	Douglas	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 4837	douglas.smyth@student.adelaide.edu.au	**PT20**
Solomon	Edward	Department of Chemistry Stanford University STANFORD CA 94305 USA	+1 650 723 9104	edward.solomon@stanford.edu	**PL5**
Somers	Neil	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9380 2413	neil@crystal.uwa.edu.au	**PM53**
Spiccia	Leone	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4528	leone.spiccia@sci.monash.edu.au	**PM2**, PM3, PM28
Steel	Peter	Department of Chemistry University of Canterbury CHRISTCHURCH NEW ZEALAND	+64 3 3642 432	p.steel@chem.canterbury.ac.nz	**K4**
Stranger	Rob	Department of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 2934	rob.stranger@anu.edu.au	**PM78**, PM79, PM80

Styles	Michelle	Department of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 7089	m.styles@pgrad.unimelb.edu.au	**PT2**
Sun	Huailin	Department of Chemistry Nankai University TIANJIN 300071 P.R. CHINA	+86 22 2350 8664	sunhl@nankai.edu.cn	**PT14**
Sutrisno		Department of Chemistry University of Newcastle CALLAGHAN NSW 2308 AUSTRALIA	02 4921 5461	chsu@alinga.newcastle.edu.au	**PM25**
Swiegers	Gerry	CSIRO Molecular Science Bag 10 CLAYTON SOUTH VIC 3169 AUSTRALIA	03 9545 2528	g.swiegers@molsci.csiro.au	**PT66**
Tiwow	Vanny	Department of Chemistry University of Newcastle CALLAGHAN NSW 2308 AUSTRALIA	02 4921 5471	cpvt@paracelsus.newcastle.edu.au	**PM24**
Todd	Jean	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 4837	jtodd@pene.science.adelaide.edu.au	**PT22**
Tolhurst	Vicki-Anne	School of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 4326	V.Tolhurst@unsw.edu.au	**PT53, PT54**

Unoura	Kei	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 1520	k.unoura@sci.monash.edu.au	**PM1**
van den Ancker	Tania	Department of Biological and Physical Sciences University of Southern Queensland TOOWOOMBA QLD 4350 AUSTRALIA	07 4631 2363	ancker@usq.edu.au	**PM19**
Vincent	Kylie	School of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 7015	k.vincent@chemistry.unimelb.edu.au	**PT10**
Vitulli	Giovanni	Department of Chemistry and Industrial Chemistry University of Pisa PISA 56126 ITALY	+39 050 918224	pervit@dcci.unipi.it	**OP45**
von Zelewsky	Alexander	Institute of Inorganic Chemistry University of Fribourg, Perolles CH-1700 FRIBOURG SWITZERLAND	+41 26 300 87 30/32	Alexander.vonzelewsky@unifr.ch	**PL9**
Wainwright	Kevin	School of Chemistry Flinders University GPO Box 2100 ADELAIDE SA 5001 AUSTRALIA	08 8201 2268	Kevin.Wainwright@flinders.edu.au	**OP2**

Wallace	Lynne	Department of Chemistry Australian Defence Force Academy CANBERRA ACT 2601 AUSTRALIA		l_wallace@adfa.edu.au	
Warden	Andrew	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 4513	andrew.warden@monash.edu.au	**PM3**
Watkins	Scott	Department of Chemistry University of New South Wales SYDNEY NSW 2052 AUSTRALIA	02 9385 5473	S.Watkins@unsw.edu.au	PT56, **PT57**
Webb	Helen	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9905 1453	helen_webb@hotmail.com	**PM8**
Wedd	Tony	School of Chemistry University of Melbourne PARKVILLE VIC 3052 AUSTRALIA	03 9344 6813	t.wedd@chemistry.unimelb.edu.au	**OP46, PT1**
Wei	Gang	School of Chemistry University of Sydney SYDNEY NSW 2006 AUSTRALIA	02 9351 4268	g.wei@chem.usyd.edu.au	PT35, **PT37, PT38**, PT39
Welling	Lee	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 3640	welling@rsc.anu.edu.au	PM60, **PM63**

Wenger	Eric	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4425	wenger@rsc.anu.edu.au	
Wheate	Nial	Department of Chemistry Australian Defence Force Academy University College University of New South Wales CANBERRA ACT 2601 AUSTRALIA	02 6268 8916	n-wheate@adfa.edu.au	**PT18**
White	Allan	Department of Chemistry University of Western Australia NEDLANDS WA 6907 AUSTRALIA	08 9380 3144		PM15, PM16, PM19, PM29, PM47, PM48, PM49, **PM51**, PM52, PM53, PM54, PM56, PM57, PT19, PT37, PT39
Whitelaw	Debra	Department of Chemistry Monash University CLAYTON VIC 3168 AUSTRALIA	03 9764 2813	Debra.Whitelaw@sci.monash.edu.au	**PM11**
Wikaira	Janice	Department of Chemistry Canterbury University CHRISTCHURCH NEW ZEALAND	+64 3364 2820	chem206@its.canterbury.ac.nz	
Wild	Bruce	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4236	sbw@rsc.anu.edu.au	PM74, PM81, PM82, PM83, PM84, PM85, PM86, PT66

Williams	Alan	Department of Inorganic Chemistry University of Geneva 30 quai Ernest-Ansermet CH 1211 GENEVA 4 SWITZERLAND		Alan.Williams@chiam.unige.ch	**K9**
Williams	Michael	School of Science Griffith University Nathan Campus BRISBANE QLD 4111 AUSTRALIA	07 3875 7728	m.williams@sct.gu.edu.au	PT60, PT61, PT62
Williams	Nicola	Monash Chemistry Wellington Road CLAYTON VIC 3168 AUSTRALIA	03 9905 5509	n.williams@sci.monash.edu.au	
Wimmer	Franz	Department of Chemistry Universiti Brunei Darussalam GADONG BE1410 BRUNEI	+67 3224 9001	fwimmer@ubd.edu.bn	**OP22, PM18**
Woodhouse	Susan	Department of Chemistry University of Adelaide ADELAIDE SA 5005 AUSTRALIA	08 8303 4837		**PT23**
Wright	James	Department of Chemistry University of Auckland Private Bag 92019 AUCKLAND NEW ZEALAND	+64 9373 7599	LJ.Wright@auckland.ac.nz	**OP17**
Yamamoto	Akio	Department of Applied Chemistry School of Science and Engineering Waseda University Shinjuku TOKYO 169-8555 JAPAN	+81 3 5286 3103	akicyama@mn.waseda.ac.jp	**OP30**

Yates	Brian	School of Chemistry University of Tasmania GPO Box 252-75 HOBART TAS 7001 AUSTRALIA	03 6226 2167	Brian.Yates@utas.edu.au	**PM55**
Young	Charles	School of Chemistry University of Melbourne VIC 3010 AUSTRALIA	03 9344 6515	c.g.young@chemistry.unimelb.edu.au	**K7**, PT6, PT7, PT8, **PT9**
Zank	Johann	Research School of Chemistry Australian National University CANBERRA ACT 0200 AUSTRALIA	02 6249 4334	zank@rsc.anu.edu.au	**PM84**, PM86
Zhou	Xiangting	School of Chemistry University College (UNSW) Australian Defence Force Academy CANBERRA ACT 2600 AUSTRALIA	02 6268 8917	zhox99@adfa.edu.au	**PT15, PT16**