



INORGANIC CHEMISTRY '86 in AUSTRALIA

Conference of the RACI Inorganic Division

Department of Inorganic Chemistry, University of Melbourne
January 28-31, 1986

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ICA'86 is the first major conference of the newly constituted RACI Inorganic Division. It follows the tradition of the twelve popular COMO meetings held over the last twenty years, but is expanded to reflect the broader interest of the Inorganic Division.

The Conference Committee wishes to acknowledge the British Council and the Wilsmore Fellowship fund of the University of Melbourne, for their support of a number of Plenary speakers at the Conference. We thank the National Australia Bank, TAA and the University of Melbourne for the provision of materials and facilities for the meeting.

ICA'86 Conference Committee

The Committee - Prof. T.A. O'Donnell (Chairman), Dr. P.A. Tregloan (Secretary), Dr. B.F. Hoskins, Dr. C.J. Marsden and Dr. R. Robson, - are all members of the Department of Inorganic Chemistry at the University of Melbourne.

A Conference Desk is set up in the foyer of the Chemistry School. All enquiries concerning registration, accommodation and the business of the Conference should be directed to members of the Committee, one of whom will try to be in attendance at most reasonable times during the meeting.

ICA'86 Programme

The programme for the meeting has been arranged around nine plenary lectures, eight session lectures and a display of a large number of posters, describing recent research in inorganic chemistry by participants and their colleagues.

The plenary and session lectures will be presented in the Masson Theatre in the Chemistry School. Access to the theatre is through the two doors on the ground floor level at the front of the theatre, or through the door at the back of the theatre on the second floor level, reached using the main stairs in the School foyer. Participants who arrive for a lecture after the advertised starting time are requested to use the back entrance to the theatre.

Lecturers who have slides or other materials for their lecture should contact the projectionist for their session through the staff at the Conference Desk in the early part of the break immediately preceding their lecture, or before 9-00 a.m. in the case of the first lecture of the day. Chairmen for lectures are requested to seek out the lecturers before their session and also advised to contact the projectionist in case there are any special arrangements or changes.

The posters will be displayed throughout the meeting in the Part 1 Laboratory, on the ground floor of the Chemistry School. Participants who are presenting posters must have them ready for display for the start of the Poster Session at 2-15 p.m. on Tuesday, January 28th. The laboratory will be open from 3-30 p.m. to 5-30 p.m. on Monday, January 27th., for those members who wish to prepare their posters in good time.

Posters have been arranged alphabetically, according to the author whose name was underlined on the abstract. In cases where there is more than one name underlined, or where there was no indication of primary responsibility for the multi-author posters, classification is by first author. An index at the end of the abstracts lists all the conference participants and any posters of which they are authors.

ICA'86 Programme, Monday, January 27

3-30

Registration, Poster Preparation

5-30

Mixer, Trinity College

7-30

ICA'86 Programme, Tuesday, January 28

	Lecture	Chairman
9-00	Opening of Conference Prof. T.W. Healy, Dean of Science, University of Melbourne	Prof. T.A. O'Donnell
	Plenary Lecture PL1 Prof. H. Taube, Stanford University "New Patterns of Reactivity in the Chemistry of Osmium Complexes"	Prof. A.M. Sargeson
10-30	<hr/> Coffee <hr/>	
11-15	Plenary Lecture PL2 Prof. W. Keim, Technical University of Aachen "Chelate Ligands in Homogeneous Transition Metal Based Catalysts"	Prof. M.I. Bruce
12-30	<hr/> Lunch <hr/>	
2-15	<hr/> Poster Session <hr/>	
3-30	<hr/> Coffee <hr/>	
4-15	Session Lectures SL1, SL2 Prof. N.S. Hush, University of Sydney "The Roles of Distance, Medium and Driving Force in Intramolecular Electron Transfer Reactions"	Prof. H. Taube
5-30	Dr. G.A. Heath, University of Edinburgh "Electrochemistry/Structure Correlations in Coordination Chemistry"	

ICA'86 Programme, Wednesday, January 29

	Lecture	Chairman
9-00	Plenary Lecture PL3 Prof. R. Hoppe Justus Liebig University, Giessen "New Routes in the Synthesis of Metal Oxides"	Prof. D.J.M. Bevan
10-30	<hr/>	
	Coffee	
11-15	Plenary Lecture PL4 Prof. R. Hoffmann, Cornell University, "The Close Ties between Organometallic Chemistry, Surface Science and the Solid State"	Prof. B.N. Figgis
12-30	<hr/>	
	Lunch	
2-15	Plenary Lecture PL5 Prof. B.G. Hyde, Australian National University, "Non-bonded Interactions and Cation Packing in Inorganic Crystals"	Prof. M. O'Keeffe
3-30	<hr/>	
	Coffee	
4-15	Session Lectures SL3, SL4 Dr. I. Grey, Division of Mineral Chemistry, C.S.I.R.O. "X-ray Diffraction Applications in Mineral Chemistry" Dr. H. Rossell, Division of Materials Science, C.S.I.R.O. " Ordering in Anion Deficient Fluorite Related Oxides "	Dr. B.M. Gatehouse
5-30	<hr/>	
7-30	<hr/>	

Conference Dinner, Trinity College

ICA'86 Programme, Thursday, January 30

	Lecture	Chairman
9-00	Plenary Lecture PL6	A/Prof. I.G. Dance
	Prof. H. Schmidbaur, Technical University of Munich, "Advances in the Chemistry of Subvalent Metals in the Late d-Block and Early p-Block with New Ligands"	
10-30	Coffee	
11-15	Plenary Lecture PL7	Prof R. Hoffmann
	Prof. J.K. Burdett, University of Chicago, "Solid State Chemistry from a Molecular Viewpoint"	
12-30	Lunch	
2-15	Plenary Lecture PL8	Prof. B.O. West
	Dr. E.N. Baker, Massey University, "Iron Binding and Transport Proteins : Structure and Function"	
3-30	Coffee	
4-15	Session Lectures SL5, SL6	Prof. C.J. Hawkins
	Dr. A.G. Wedd, LaTrobe University "Generation of cis-[Mo(V)-O-(OH)] and cis-[Mo(V) O ₂] Centres : ¹ H- and ¹⁷ O- Superhyperfine Coupling Parameters Relevant to Molybdo-enzymes"	
	Dr. S.F. Lincoln, University of Adelaide "Structural and Mechanistic Studies of Inclusion Complexes formed by Cryptands and Cyclodextrins."	
5-30		

ICA'86 Programme, Friday, January 31

	Lecture	Chairman
9-00	Plenary Lecture PL9	Prof. H. Schmidbaur
	Prof. B.L. Shaw, University of Leeds, "New Developments in the Chemistry of Bimetallic Systems"	
10-30	<hr/> Coffee <hr/>	
11-15	Session Lectures SL7, SL8	Dr. L.F. Lindoy
	Dr. S.B. Wild, Australian National University "Macrocyclic Ligands Containing Resolved Arsenic Donors"	
	Prof. B.H. Robinson, University of Otago "Synthesis and Electron Transfer Properties of Acetylene-capped Clusters"	
12-30	<hr/> Lunch <hr/>	
2-15	Divisional Meeting	Dr. M.A. Bennett
	Burrows Lecture PL10	Dr. M.A. Bennett
	Prof. B.N. Figgis, University of Western Australia, "The Metal Ligand Bond Revisited Experimentally"	
3-45	Closing of Conference	Prof. T.A. O'Donnell

NEW PATTERNS OF REACTIVITY IN THE CHEMISTRY OF OSMIUM COMPLEXES

Henry Taube,
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Stanford University,
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The work to be described is an outgrowth of the studies over more than two decades devoted to ruthenium in the lower oxidation states. Osmium differs from its congener in several important ways. The two that provided the motivation for the studies to be described are: the higher oxidation states are more stable than they are for ruthenium, and back-bonding is much more prominent for Os(II) than it is for Ru(II). Two kinds of studies will be described which are in line with the first expressed interest: activation of the Os(VI)-N³⁻ bond in [Cl₄OsN]⁻ brought about by changing the auxiliary ligand (among other reactions, a facile coupling to form the N≡N bond will be described) and developing the chemistry of Os(III) and Os(IV) in the biscyclopentadienide system. In line with the last stated interest, experiments will be described which demonstrate a remarkably high reactivity of the moiety (NH₃)₅Os(II) for solvents which are ordinarily considered to be rather unreactive.

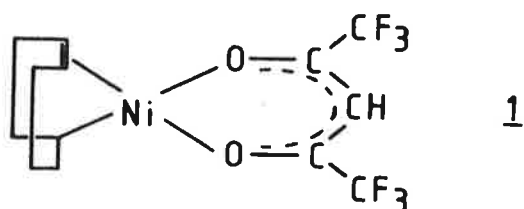
"Chelate Ligands in Homogeneous, Transition Metal Based Catalysis"

W. Keim,

Institut für Technische Chemie und Petrolchemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, Worringer Weg 1,
D - 5100 Aachen (FRG)

Since many years we are interested in the oligomerization of mono olefins by nickel complexes. For our catalyst selection square planar nickel complexes possessing chelate ligands with donor and acceptor properties were chosen [1-3].

The reaction of $(COD)_2Ni$ with the chelate ligand $CF_3COCH_2COCF_3$ yielded the square planar complex 1, which is an excellent catalyst for the linear dimerization of α -olefins [4].



Data will be presented, showing the impact of the chelate ligands in 1 on the catalytic properties.

A series of square planar complexes could also be synthesized according to Figure 1 [5].

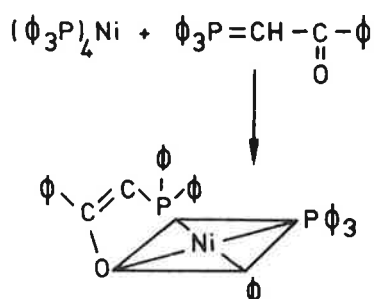
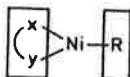


Figure 1. Synthesis of square planar nickel complexes with $P \curvearrowright O$ -chelates

Toluene solutions of these complexes react at 90°C and 50 bar pressure with ethylene, yielding oligomers of 99 % linearity and > 98 % α -olefin content. All complexes are active in Shell's SHOP process, which is used in two plants to manufacture α -olefins.

Besides $O \curvearrowright O$ - and $P \curvearrowright O$ -chelates $As \curvearrowright O$ - and $N \curvearrowright P \curvearrowright N$ -ligands will be discussed analyzing their steering influence in olefin oligomerizations.

Evidence will be provided that besides the chelate part in complex of type 2 also the R-part is essential in determining catalytic properties.



2

$\begin{pmatrix} x \\ y \end{pmatrix} = \text{chelate}$

R = alkyl, allyl, olefin

References

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- 2 W. Keim, "Fundamental Research in Homogeneous Catalysis", Plenum Press, Vol. 4, 131-145 (1984).
- 3 W. Keim, in "Catalytic Transition Metal Hydrides", Annals of the New York Academy of Sciences, Vol. 415, 191-201 (1983).
- 4 W. Keim, B. Hoffmann, R. Lodewick, M. Peuckert, G. Schmitt J. Fleischhauer, U. Meier, J. Of Molec. Catalysis 6, 79-97 (1979).
- 5 F.H. Kowaldt, C. Krüger, W. Keim, Angew. Chem. 90, 6, 493 (1978).

NEW ROUTES IN THE SYNTHESIS OF METAL OXIDES

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Solid state chemists have difficulties in expressing accurately what they know because Berzelian language of formulas is inadequate (e.g. TiO_x) and is used as a "crutch". New concepts are needed urgently.

We have converted Niggli's static description of structural facts into a dynamic possibility to predict unexpected oxides like $\text{CsK}_4[\text{GaO}_4]$, although $\text{K}_5[\text{GaO}_4]$ is unknown. Exchange reactions provide us with new metal oxides not in thermodynamic equilibrium (e.g. single crystals of HT- Li_2PbO_3 below $T(\text{trans.})$). The concept of soy allows preparation of many new oxides at relatively low temperatures. Sometimes it is necessary to prepare "virginal" oxides. (e.g. BaO from BaHg via BaHgO_2).

Other questions to be mentioned are:

How to cut "chains" on chemical "battleships"? How to cut rings and vice versa? How to disaggregate or to polymerize? And other items of molecular-like reactions in solid state chemistry.

Can we avoid 'reactions with wall' working in closed systems? Or is it possible to use these "feared" complications in the form of new pathways of synthesis? So we deal with the oxidation of metals ($2\text{Na}_2\text{O}_2 + 4\text{Ag} = \text{Na}_4[\text{Ag}_4\text{O}_4]$) or intermetallic compounds like NaIn, leading to the first In_5 -cluster in $\text{Na}_{24}[\text{In}_5]\text{O}_{15}$, the first oxoaurate(I) with XeF_2 -like anions, $\text{KNa}_2[\text{AuO}_2]$, tailor-made $\text{KNa}_2[\text{CuO}_2]$, etc. $\alpha\text{-Li}_6\text{UO}_6[\text{Vac}]$ with vacancies L cries for "stuffed" derivatives, here $\text{KLi}_5[\text{IrO}_6]$. Other problems of vacancies occur with Na_3TlO_2 (from $\text{NaTl} + \text{Na}_2\text{O}_2$).

THE CLOSE TIES BETWEEN ORGANOMETALLIC CHEMISTRY, SURFACE SCIENCE,
AND THE SOLID STATE

Roald Hoffmann

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Abstract. There can be no real divergence between the bonding in a discrete molecule and that in an extended two- or three-dimensional solid. Translational symmetry introduces some complications, a different language, but also some simplifications. The essential continuity of bonding descriptions between organometallic chemistry, surface science and the rich world of three-dimensional extended systems becomes evident when one uses the language of densities of states and various partitions thereof. Examples drawn from bulk interstitial carbides and CO on surfaces will illustrate these ideas.

NON-BONDED INTERACTIONS AND CATION PACKING IN INORGANIC CRYSTALS

B.G. Hyde

Research School of Chemistry, A.N.U.

The "ionic model" with its paraphernalia of ion radii and radius ratio rules has been the accepted paradigm in crystal chemistry for most of the last 60 years. Recently, sophisticated quantum mechanical methods have also been successfully applied with some important consequences, especially the elimination of the boundary between molecular and non-molecular structures. But the latter covers only a part of the field: the more complex structures and structural systematics remain largely untouched. So there is still a place for simpler notions even if, like the "ionic model", they are relatively crude and unsophisticated.

The "ionic model" is severely inadequate, and M. O'Keeffe and I have been exploring an equally simple hypothesis, relatively untried for crystals, that non-bonded interactions (especially between second-nearest-neighbour atoms) are at least as important as the interactions between nearest neighbours. Our emphasis is particularly on cation-cation interactions, although those between anions (traditionally considered to dominate) are not ignored. An important parameter in determining the relative importance between these two is the stoichiometric ratio of cations to anions, previously largely ignored.

This alternative approach will be discussed, as manifested in a number of directions: (1) in determining crystal structures and coordination numbers; (2) in its effect on the thermodynamic stability of some simple inorganic compounds; (3) in leading to simple descriptions of the structures of some common, simple inorganic compounds such as metal sulphates; previously undescribed, and apparently outside the ambit of solid state chemists but (4) in the last few years of great interest to solid state physicists because at least some of them exhibit the (initially surprising but now fashionable and, I believe, fundamentally important) phenomenon of modulated ("incommensurate") structures in certain temperature ranges; (5) in accounting for the effect of high pressure on crystal structure.

**Advances in the Chemistry of Subvalent Metals in the Late
d-Block and Early p-Block with New Ligands.**

Hubert Schmidbaur

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1,3-difunctional organophosphorus ligands with chelating or bridging moieties containing the C-P-C and/or P-C-P skeleton form a variety of complexes with gold in its classical oxydation state +I. In these compounds, the metal atoms are not only held in close geometrical proximity by the small-bite ligands, but are also notably attracted towards each other through interactions which are based on relativistic effects. Molecular conformations which are unfavourable in standard situations, become energetically favourable through Au-Au contacts. The phenomena are obvious in the structural parameters, as determined by single crystal X-ray diffraction, and in UV/VIS and ^{197}Au Mössbauer spectra.

Additional evidence is obtained from a study of the chemical reactions. A series of oxydative addition processes have been shown to occur in discrete steps involving true metal-metal bonded species based on the unusual oxydation state +II of gold. The final products are cyclic or polycyclic binuclear Au(III) compounds, which are subject to clear-cut thermal reductive elimination in favourable cases. Work along these lines is also in progress in the laboratories of J.P. Fackler (Texas A&M) and M.A. Bennett (ANU-RSC Canberra).

Further studies have focused on the directing influence of the weak interactions between closed-shell (d^{10}/d^{10}) centers on the positioning of other substituents attached to the metal atoms. Both T-shaped and Ψ -square-planar arrays have been found for gold(I). It appears that all these effects represent cases of "weak bonding" which is quite susceptible even to subtle changes in the geometry and the nature of the ligands.

(Page 2, H. Schmidbaur)

Univalent gallium, indium, and thallium are characterized by the electronic configuration $d^{10}s^2$, and thus differ from the univalent coinage metal cations by the presence of a filled s-orbital. These orbitals are subject to a significant Relativistic Contraction, while the underlying p- and d-orbitals are energetically destabilized. (Relativistic Self-Consistent Expansion: Pyykkö, Desclaux, Accounts Chem. Res. 12, 267 (1979).) Among a series of effects possibly associated with this modified atomic configuration are new findings in the chemistry of arene complexes. Ga(I), In(I), and Tl(I) have been found to form stable arene adducts with either one or two η^6 -bonded benzene molecules. A variety of structures has been determined by X-ray diffraction, including cyclic and cage-like oligomers, chain-polymers, and three-dimensional coordination networks. Methylated arenes, like mesitylene or hexamethylbenzene, are the preferred ligands in mixed systems, as suggested by $^{69}\text{Ga}/^{71}\text{Ga}$ NMR spectra and competition experiments.

Polyarene ligands, like α,ω -diphenylalkanes, vicinal diphenylcyclopropanes, or phenylated ethylenes, accommodate the univalent metal cations between mutually inclined arene rings, which are again η^6 -bonded. Finally, cyclophanes with different loop-sizes between the arene rings were also found to form adducts with the low-valent Group IIIb (IUPAC: Group XIII) cations. Some of these adducts are extremely insoluble in organic solvents and can be used for complete precipitation of the subhalides, which are otherwise exceedingly soluble in aromatic hydrocarbons.

The new systems are of interest for the extraction and purification of gallium metal, for homogeneous reduction, and for the activation of arenes for electrophilic substitution.

The author is indebted to a large number of colleagues and students for their skilful and enthusiastic work and for many helpful discussions. Support by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Hoechst AG, Degussa AG, Siemens AG, and Preussag AG is gratefully acknowledged.

SOLID STATE CHEMISTRY FROM A MOLECULAR VIEWPOINT

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We can today perform a band structure computation on crystalline solids which differ considerably in complexity. If the unit cell size is small these can be quite good calculations which can accurately locate the lowest energy structure, its cohesive energy and dimensions from amongst its competitors. Whatever the size of the system under study however, we always face a taxing problem. Given a pile of computer output, how do we extract the essence of the electronic structure problem from these numbers to provide an understanding of the system under discussion? The crafting of explanations and the construction of simple models is at the heart of the challenge offered us by the diversity of solid state structure types.

Two systems will be discussed which will show how insight may be gained into solid state structural problems by relating structural-electronic effects to those occurring in molecules. One study, that of the origin of Pauling's rules, looks at systems where localized hybrid orbitals are traditionally used in describing their electronic structure. The other, aimed at trying to understand the variation of the stable crystal structure of the transition elements across the series, is in an area where a delocalized picture of the bonding is usually used. By going back and forth between molecules and solids simple models result which are useful ones for understanding the more complex picture presented by solids.

Iron Binding and Transport Proteins : Structure and Function

E.N. Baker

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Massey University, Palmerston North, New Zealand.

The fascination of bioinorganic chemistry is well illustrated by the biochemistry of iron. Its particular properties in aqueous solution have resulted in the evolution of a variety of ways of handling and using iron by proteins. Iron proteins can be somewhat arbitrarily subdivided into proteins of iron storage (ferritin), proteins in which iron atoms are intrinsic and required for function (haemoglobin, cytochromes etc.) and proteins of iron binding and release (transferrins).

Detailed structural data are available for proteins in the first two classes, and many aspects of their functions are understood, through the integration of a wide variety of approaches. This lecture will focus primarily on the third class, as exemplified by the transferrins¹, because (i) they have hitherto been less well characterised, as regards structure, (ii) they form a functional link between the other two classes, and (iii) they provide intriguing examples of biological coordination chemistry.

The transferrin family includes serum transferrin, ovotransferrin (egg white) and lactoferrin (milk and other secretions). All are monomeric glycoproteins, with molecular weights of about 80,000, and two specific binding sites for Fe(III) (with two associated anion-binding sites) per molecule. Their main functions are probably (i) reduction of the "free" iron concentration, and (ii) iron transport, the relative importance depending on biological location, and on variations in their metal-binding ability. This will be illustrated with respect to lactoferrin and serum transferrin.

Amino acid sequence comparisons show a remarkable homology both between species and between the N-terminal and C-terminal halves of each molecule (the result of gene duplication).² Low resolution crystallographic studies have revealed in each case a molecule divided into two distinct globular lobes. These can be separated by mild proteolysis, and each is found to contain one iron binding site. Some very recent crystallographic results on lactoferrin, both a higher-resolution study (3.5Å), and the crystallisation of other forms of lactoferrin, will be presented.

Attempts to determine the nature of the iron sites will be discussed. The importance of cation size and charge are apparent, and a variety of spectroscopic studies, together with metal-substitution experiments, model studies, and amino acid sequence comparisons, in a number of laboratories, have led to a consensus model of 2 or 3 phenolate oxygens (from Tyr), 2 imidazole nitrogens (His), one HCO_3^- ion, and possibly one water (or OH^-) as ligands.^{2,3}

A large number of experiments have also been directed towards the mechanisms of iron binding and release. A characteristic feature of the transferrins is the synergistic relationship between anion(HCO_3^-)-binding and cation(Fe^{3+})-binding. There is evidence for a conformational change accompanying binding, while release is mediated by pH and possibly by interaction with other species. Of particular interest is the competition with other chelators such as citrate and the siderophores produced by bacteria.

Finally there are important general questions, such as whether any non-equivalence of the iron sites is functionally-significant, and what the advantages are (if any) in a two-sited protein.

Overall, bioinorganic chemistry owes a great deal to the amalgamation of many varied approaches. A new and exciting possibility is offered by recent advances in molecular biology and this too will undoubtedly make an impact on this field.

1. Two recent reviews are (a) Chasteen, N.D. (1983), in "Iron Binding Proteins, Without Cofactors or Sulphur Clusters", ed. Theil, E.C. et al, pp. 202-233, Advances in Inorganic Biochemistry series, Elsevier Press, (b) Brock, J.H. (1985) in "Topics in Molecular and Structural Biology. Metalloproteins Vol. II", ed. Harrison, P.M., Macmillans.
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3. Pecoraro, V.L., Harris, W.R., Carrano, C.J. and Raymond, K.R. (1981). Biochemistry 20, 7033, and references therein.

NEW DEVELOPMENTS IN THE CHEMISTRY OF BIMETALLIC SYSTEMS

BERNARD L SHAW

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New methods of synthesizing heterobimetallic systems containing bridging $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) are described i.e. complexes containing the moiety $\text{M}^1(\mu\text{-dppm})_2\text{M}^2$. Four general methods of synthesis have been devised (1) REDOX, (2) Using monodentate dppm complexes, (3) Ring-opening reactions, and (4) Transmetallation, enabling many hetero- and homo-bimetallic systems containing $\text{M}^1(\mu\text{-dppm})_2\text{M}^2$ moieties to be synthesized. M^1 and M^2 can be drawn from Cr, Mo, W, Mn, Re, Os, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Cd or Hg: associated ligands include $\text{C}\equiv\text{CR}$, $\text{C}\equiv\text{N}$, $\text{C}\equiv\text{NR}$, halides, alkyl, aryl, H, CO, $\text{RC}\equiv\text{CR}$. Many of the complexes are fluxional and *trans*-, *cis*- and other stereochemistries are exhibited by the metals. Various reactions of these complexes are described.

THE METAL-LIGAND BOND REVISITED EXPERIMENTALLY

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The history of gaining understanding of the transition-metal ligand bond is traced briefly. The distinction between the type of information given by "spectroscopic" techniques (including e.s.r., magnetism and n.m.r.) relating essentially to energetic considerations on the one hand, and given by diffraction methods, relating to spacial extent, on the other hand, is set out.

The relationship between the information given by the charge distribution (X-ray diffraction) and by the spin distribution (polarised neutron diffraction) is outlined. The spin distribution is influenced by the short-range (nearest neighbour) effects of covalency. The charge distribution reflects these, but also short-range and long-range effects of electrostatic polarisation, and these are dominant in all but highly covalent systems.

The charge movements due to the covalent contribution to the bonding may probably be fairly well described by conventional molecular orbital treatments, simple for ionic systems, more sophisticated for covalent ones. However, it seems that those are inadequate for dealing with the spin distributions in the latter cases. There the effects of interelectronic repulsions (expressed often as "configurational interaction") may be comparable with those from covalency.

To take advantage of all the information in the spin densities will probably require the C.I. calculations which are just now becoming possible for transition metal systems. A major challenge will be to make such results understandable in simple chemical terms.

THE ROLES OF DISTANCE, MEDIUM AND DRIVING FORCE IN INTRAMOLECULAR ELECTRON TRANSFER KINETICS

N. S. Hush,
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University of Sydney,
Sydney, N.S.W. 2006, Australia.

Intramolecular electron transfer in systems in which donor and acceptor are linked by conjugated bifunctional ligands providing an electronic 'pathway' have been studied in much detail, most notably and completely by H. Taube. Systems in which the linkage is apparently electronically insulating and might be thought to function only as a geometrical 'spacer' have only recently begun to be investigated in detail, despite work again by Taube and co-workers which indicated that a conjugated pathway is not a necessary condition for quite rapid transfer. This is clearly of importance for interpretation of biological electron transfer processes, which often take place over large distances.

Central issues are: dependence of transfer rate on distance and electronic structure of the linkage; influence of the medium, and the role of the overall driving force. In order to obtain measurements on systems whose properties can be systematically varied and whose geometries are closely defined, we have undertaken a programme in which series of rigidly linked donor-acceptor systems with a plane of symmetry, in which distance can be incrementally varied, are designed, synthesized and experimentally and theoretically investigated. One example is the series of which I, below, is the '8-bond' member:



The principal participants are: M.N. Paddon-Row and his synthetic group (Sydney); J. Verhoeven and H. Oevering (Amsterdam: picosecond emission); J. Warman (Delft: TRMC); and J. Miller (Argonne: pulse radiolysis). Electrochemistry is being studied by P. Lay (Sydney).

For the above series, it is found that for linear separations up to 10.7 Å, photoinduced transfer occurs with $\tau < 10$ picosecond (the resolution limit); at 18.5 Å, τ is ~ 10 nanosecond. These rates are about 3 orders of magnitude faster than those recently reported by J. Miller for steroid-linked ground-state transfers of the type $A^- - B \rightarrow A - B^-$. So far the analogous pulse radiolysis work on our above series yields only a lower limit ($\tau < 10^{-9}$) as rates are too rapid to measure exactly. The photoinduced rates vary by a factor of only 2.5 for solvents ranging from cyclohexane to acetonitrile. These results, although perhaps surprising, follow the predictions of relatively simple electron-transfer theory.

Structure/Electrochemistry Correlations in Coordination Chemistry
by Graham A. Heath. University of Edinburgh

The redox processes available in coordination complexes are intimately linked to their molecular and electronic structure. Electrochemical methods provide a direct means for exploiting these properties thus mapping the frontier orbitals and, by electrosynthesis, characterising otherwise inaccessible oxidation states. "Spectro-electrochemical" techniques, for example, avoid the necessity of isolating unstable products and permit their study *in situ*. Two contrasting topics will be used to illustrate the above ideas:

In the stepwise reduction of $[\text{Ru}(\text{bipy}^\circ)_3]^{2+}$ (I) and similar complexes, spectro-electrochemical techniques point forcefully to localisation of each added electron on an individual ligand, to form successively $[\text{Ru}(\text{bipy}^\circ)_2(\text{bipy}^-)]^+$ (I^-), $[\text{Ru}(\text{bipy}^\circ)(\text{bipy}^-)_2]$ (I^{2-}) and $[\text{Ru}(\text{bipy}^-)_3]^-$ (I^{2-}). The unexpected asymmetric charge-distribution in the intermediate complexes, I^- and I^{2-} , is confirmed by observable ligand-based inter-valence phenomena. Similarly, the crucial luminescing charge-transfer state I^* is now believed to adopt spontaneously the configuration $^*[\text{Ru}^{\text{III}}(\text{bipy}^\circ)_2(\text{bipy}^-)]^{2+}$, despite the strictly D_3 nature of I in the ground state. The remarkable structural and spectroscopic analogies between the optically excited and electro-generated species will be examined.

The hexahalometallates of 4d and 5d transition elements provide an extensive family of compounds in which the properties of simply co-ordinated heavy metal ions can be explored, particularly in their higher valencies. Successive E° values for the couples $[\text{MF}_6]^{z/z-1}$ ($z=0,-1,-2$), where $\text{M} = \text{Nb}, \text{Mo}, (\text{Tc}), \text{Ru}$ and Ta to Ir , in ultra-dry CH_3CN follow remarkable linear trends related to periodic progression in central ion core charge and electronic configuration. Latterly, comprehensive data for the corresponding hexachloro-metallates $[\text{MCl}_6]^{z/z-1}$ ($z=0,-1,-2,-3$), where $\text{M} = \text{Zr}$ to Pd and Hf to Pt , have amplified this orderly behaviour and confirmed the possibility of quantifying nephelauxetic effects etc from electrochemical measurements. These discoveries appear to have very general significance for descriptive transition metal chemistry.

X-ray Diffraction Applications in Mineral Chemistry

I.E. Grey and I.C. Madsen

CSIRO Division of Mineral Chemistry

A review will be given of current research at the CSIRO Division of Mineral Chemistry, involving application of X-ray diffraction techniques to problems in mineral processing and mineralogy. Powder X-ray diffraction is provided as a service facility in the Division. It is used to routinely identify phases in complex mixtures, in conjunction with the PDIDENT search and match programs and the JCPDS powder diffraction data base. These are implemented on the Division's VAX 750 computer. Programs have been developed for quantitative phase analysis in complex mixtures of industrial phases and of minerals. The Rietveld profile refinement technique has been extensively developed (by R.J. Hill) and examples of its application will be given. High temperature powder diffraction studies up to 2500°C can be carried out on a Rigaku θ - θ diffractometer equipped with platinum and/or tungsten heaters. Step-scan intensity data for structure refinements at temperatures up to 400°C can be collected on a Philips diffractometer. The high-temperature facilities are used for establishing phase diagrams at temperature, especially in systems containing unquenchable structures; for studying dehydration/dehydroxylation and decomposition reactions and for determining structural changes as a function of temperature.

Single-crystal diffraction equipment used includes standard film methods (precession, Weissenberg), and two single-crystal diffractometers. The structural group specialises in the structures of oxide phases exhibiting short-range order, incommensurate structures, long-period intergrowths and crystallographic shear, and on the characterisation and classification of oxide and sulphosalt (W.G. Mumme) minerals.

Examples will be given of application of diffraction techniques to problems in minerals and manufacturing industry (lead-acid batteries, regeneration of caustic from pulp black liquors, ilmenite-processing, lead cementation) and to the characterisation of new minerals and synthetic compounds.

ORDERING IN ANION-DEFICIENT FLUORITE-RELATED OXIDES

H.J. Rossell,

CSIRO Div. of Materials Science, Normanby Rd., Clayton 3168.

The various atomic ordering processes known to occur in oxides of the fluorite structure $\text{MO}_{2-x} \square_x$ (M = one or more cations of various valence, \square = anion vacancy) are reviewed and discussed in terms of the principles of crystalline constitution that apply in other materials of variable composition. The long-range ordered fluorite-related superstructure phases exhibit complete ordering of the formal anion vacancies together with various degrees of cation ordering. The vacancies always associate in pairs separated by a $1/2[111]$ fluorite lattice vector to produce MO_6 octahedra in place of the parent MO_8 cubes. In the various superstructures, the arrangements of these octahedra and the cation ordering schemes are linked, since it is the smallest available cation type that assumes octahedral coordination by O. The defect fluorite phase, exemplified by cubic stabilized zirconia, does not have the random distribution of cations and of anion vacancies that is commonly asserted, but instead the cations and formal anion vacancies are ordered as in one of the superstructures, but only over microdomains about 20-50Å in diameter; microdomains occur in all possible orientations of the superstructure ordering pattern that preserve the common fluorite-type basis structure.

GENERATION OF $cis-[Mo^V O(OH)]$ AND $cis-[Mo^V O_2]$ CENTRES: 1H - AND ^{17}O -SUPERHYPERFINE COUPLING PARAMETERS RELEVANT TO MOLYBDO-ENZYMES

by Frank Farchione, Graham L. Wilson, Graeme R. Hanson, Clyde G. Rodrigues, Trevor D. Bailey, Raman N. Bagchi, Alan M. Bond, John R. Pilbrow and Anthony G. Wedd

La Trobe, Deakin and Monash Universities

The complex molybdenum hydroxylases such as xanthine oxidase, sulfite oxidase and nitrate reductase feature various active centres (Mo, Fe_2S_2 , heme, flavin, Se) arranged as internal electron transfer chains. However, substrate oxidation occurs at the molybdenum sites and ^{95}Mo , 2H and ^{17}O isotope substitution permits identification of 1H - and ^{17}O -superhyperfine coupling in the various ESR-active forms of the enzymes. Ligand oxo, OH, OH_2 and OR (where R is derived from substrate) are possible sources of the coupling.

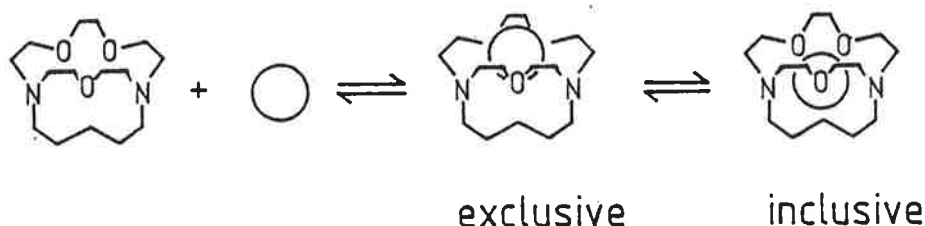
The present work aims to place oxygen and hydrogen atoms in stereochemically-defined positions relative to a Mo^V centre and its magnetic orbital. Electrolysis of $cis-[Mo^{VI} O_2 L]$ ($LH_2 = (HSCH_2CH_2N-(MeCH_2)_2)$) at -1.4 V vs SCE IN CH_2Cl_2 at $-42^\circ C$ in the cavity of an X-band ESR spectrometer generates $cis-[Mo^V O_2 L]^-$ which, in the presence of H_2O , converts to $cis-[Mo^V O(OH)L]$. 1H - and ^{17}O -superhyperfine coupling constants of 13.7 and $7(\pm 2) \times 10^{-4} \text{ cm}^{-1}$ respectively are observed for $cis-[Mo^V O(OH)L]$ and strongly support the presence of an OH ligand at the ESR-active sites of sulfite oxidase, nitrate reductase and desulfo xanthine oxidase. Related experiments involving species such as $[Mo^{VI} O(SPh)_4]^-$ and $[Mo^V OCl_2(^{17}O-C_6H_4-CH=N-C_6H_4-^{16}O)]^-$ will be discussed.

STRUCTURAL AND MECHANISTIC STUDIES OF INCLUSION COMPLEXES FORMED BY CRYPTANDS AND CYCLODEXTRINS.

Stephen F. Lincoln.

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University of Adelaide, Adelaide, South Australia 5001.

Inclusion processes whereby a metal ion or molecule is included partially or totally within a molecular cavity are of both intrinsic interest and of biological importance. In this discussion the inclusion of metal ions is illustrated by our research into the complexation of alkali metal ions by cryptands (polyoxadiazabicycloalkanes [1]) to form cryptates as shown below for C21C₅. It is found that in the solid state and in solution the sodium cryptates formed with both C21C₅ and C211 (in which



the middle -CH₂- of the (-CH₂-)₅ ring of C21C₅ is replaced by O) form exclusive cryptates in which the sodium ion resides on a face of the cryptand; whereas with lithium ion exclusive cryptates are formed in which the lithium ion resides in the centre of the cryptand cavity. These structural differences coincide with profound differences in the lability and stability of the cryptates. The mechanistic origins of these differences will be discussed.

Our research on the inclusion of various molecules by α-, β- and γ-cyclodextrins (α-1,4-linked cyclic oligomers of D-glucopyranose)[2] will be used to illustrate the inclusion of molecular species and also the effect of the size of the cyclodextrin cavity on the structure and formation mechanism of the cyclodextrin inclusion complex.

[1] J.M.Lehn, *Acc.Chem.Res.*, 1978, 11, 49.

[2] M.L.Bender and M.Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, Berlin, 1978.

MACROCYCLIC LIGANDS CONTAINING RESOLVED ARSENIC DONORS.

S. Bruce Wild, Research School of Chemistry, Australian National University, Canberra, A.C.t. 2601.

Optically active quadridentate macrocycles containing resolved tertiary arsine donors have been prepared for the first time. The molecules are members of a new family of 14-membered rings with trans-disposed like pairs of imino, secondary amino, or thioether donors, in addition to a pair of asymmetric arsenic donors. Stereospecific syntheses of each of the two possible diastereomers of each ligand will be described, as well as some quantitative asymmetric transformations between the diastereomers of each macrocycle in the free and coordinated state. A novel and apparently general relationship between 14-membered macrocyclic diimines of this type and the corresponding 7-membered benzazepines will be revealed. The new macrocycles are powerful chelates for the stereospecific chelation of 'soft' metals. The syntheses highlight the utility of metal complexation as a means of modifying and controlling organic reactivity. Aspects of optical resolution, protection, and the stereocontrol of dimerization of heavily functionalized arsine precursor molecules by palladium(II) complexes will be discussed.

SYNTHESIS AND ELECTRON TRANSFER PROPERTIES OF ACETYLENE/CAPPED CLUSTERS

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New Zealand.

Polyacetylene doped with appropriate acceptors and donors has been shown to have interesting electron transfer properties. This paper describes the systematic synthesis and electron transfer properties of some precursors of polyacetylene complexes containing the tricobalt carbon cluster $\text{CCo}_3(\text{CO})_9$. Cadiot-Chodkiewicz coupling between $\text{BrCCo}_3(\text{CO})_9$ and $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{Ph}, \text{Me}_3\text{Si}, \text{H}$) or reaction between $\text{RC}\equiv\text{CMgBr}$ and $\text{BrCCo}_3(\text{CO})_9$ gives brown $\text{RC}\equiv\text{CCCo}_3(\text{CO})_9$. $\text{Co}_2(\text{CO})_8$ reacts with the acetylene function giving green $\mu\text{-}[(\text{CO})_9\text{Co}_3\text{CC}\equiv\text{CR}](\text{-Co}_2(\text{CO})_6)$. $\text{RC}\equiv\text{CCCo}_3(\text{CO})_9$ ($\text{R} = \text{Ph}$ not Me_3Si) rearranges spontaneously to a cyclopentadienone complex $[(\text{CO})_9\text{Co}_3\text{C}]_2\text{-}[\eta^2\text{-C}_4\text{H}_4\text{CO}]$. Complexes with larger alkyne chains, e.g. $(\text{CO})_9\text{Co}_3\text{CC}\equiv\text{C-C}\equiv\text{CCCo}_3(\text{CO})_9$ etc, have also been synthesised. From the reactions with $\text{R} = \text{H}$ a black shiny insoluble material was isolated which can be formulated as a polyacetylene $(\text{CCo}_3(\text{CO})_9)_n$ complex. X-ray structural and spectroscopic data on the electron delocalization from the cluster redox centre through the acetylene chain will be correlated with the electron transfer properties determined by electrochemical methods.

PHOSPHINE ADDUCTS OF CADMIUM AND MERCURY
XANTHATES AND HALOXANTHATES

B.F. Abrahams, M. Corbett, D. Dakternieks, B.F. Hoskins,

E.R.T. Tiekink and G. Winter

Department of Inorganic Chemistry, University of Melbourne,
Parkville, 3052

Haloxanthate complexes $M(^i\text{Prxan})X$ ($M = \text{Cd}, \text{Hg}$; $X = \text{Cl}, \text{Br}, \text{I}$) have been isolated and appear to be polymeric. Multinuclear NMR data show that mercury haloxanthates react with tertiary phosphines to give 1:1 adducts $\text{HgX}(^i\text{Prxan})(\text{phos})$ in solution. The cadmium complex $\text{CdI}(^i\text{Prxan})$, however, reacts differently with phosphines and gives $\text{CdI}_2(\text{phos})$ and $\text{Cd}(^i\text{Prxan})_2(\text{phos})$ in solution.

The crystal structures of $\text{Cd}(^i\text{Prxan})_2(\text{PPh}_3)$, $\text{Hg}(^i\text{Prxan})_2(\text{Pcyc}_3)$ and $\text{Hg}(^i\text{Prxan})_2(\text{PPh}_3)$ all show approximate trigonal-bipyramidal environments about the central metal which, in each case, include a long metal-sulphur interaction. Comparisons with structures of the parent bisxanthate complexes imply that the long metal-sulphur interactions occur as a consequence of the metal atom's tendency to increase their coordination number in the presence of phosphorus and sulphur donor atoms.

COPPER PROMOTED REACTIONS OF THE HETEROCYCLIC
THIOAMIDE, 2-THIAZOLIDINETHIONE

ERIC W. AINSCOUGH, BRYAN F. ANDERSON, EDWARD N.
BAKER, ALISTAIR G. BINGHAM, MARK L. BRADER, and
ANDREW M. BRODIE

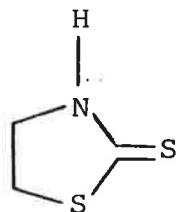
Department of Chemistry and Biochemistry, Massey
University, Palmerston North, New Zealand.

GRAEME J. GAINSFORD

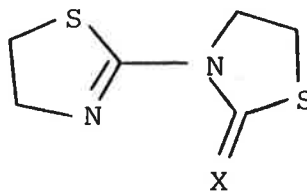
Chemistry Division, D.S.I.R., Petone, New Zealand.

ABSTRACT

The heterocyclic thioamide, 2-thiazolidinethione (L^1H) reacts with copper(II) salts in nitromethane solution to yield complexes of the new chelating ligands 3-(4,5-dihydro-2-thiazolyl)-2-thiazolidinethione (L^3), *viz.* $[(CuL^3Cl_2)_n]$, $[CuL^3Br]$ and $[CuL^3_2]ClO_4$, or its carbonyl analogue, 3-(4,5-dihydro-2-thiazolyl)-2-thiazolidinone (L^2), *viz.* $[CuL^2_2(H_2O)_2](ClO_4)_2$. A possible mechanism for these reactions will be briefly discussed along with the single crystal x-ray structures for these compounds.



L^1H



$L^2 \quad X = O$

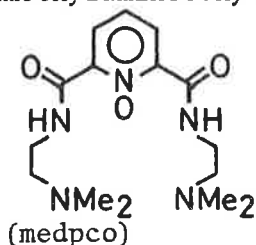
$L^3 \quad X = S$

METAL COMPLEXES WITH A POTENTIALLY BINUCLEATING N-OXIDE LIGAND

Michael Antolovich, David J. Phillips and A. David Rae

School of Chemistry, University of N.S.W., P.O. Box 1, Kensington, NSW, 2033.

Simple pyridine N-oxide ligands are well studied, and produce many N-oxide-bridged copper(II) complexes. Binucleating N-oxide ligands are, however, rare. We have been studying N,N'-bis(2-N,N-dimethylaminoethyl)-pyridine-2,6-dicarboxamide 1-oxide (medpco), a



potentially binucleating N-oxide ligand. We have obtained 1:1 complexes of medpco with nickel(II) and copper(II). Also produced was $\text{Cu}_2(\text{medpco})\text{Cl}_4$. The physical properties of this 2:1 complex do not support N-oxide bridging. An X-ray structure determination confirms this. One copper occupies an ONN ligand site and is doubly chloride-bridged to a second external copper which is also bonded to two terminal chlorides.

The second ligand donor site in $\text{Cu}_2(\text{medpco})\text{Cl}_4$ is blocked by amide hydrogen-bonding. We therefore deprotonated medpco, using Et_3N , and obtained $\text{Cu}_2(\text{medpco}-2\text{H})\text{Cl}_2$. This complex displays no magnetic interaction, but an X-ray structure determination shows a binucleated structure, with an N-oxide and two chloride bridges. One copper is displaced from the ligand plane and this may reduce super-exchange via the N-oxide group and minimise magnetic interaction.

With copper(II) tetrafluoroborate in methanol the complex $\text{Cu}(\text{medpco})(\text{BF}_3\text{OCH}_3)\text{BF}_4$ was obtained. The X-ray structure analysis shows a rare example of bridging BF_4^- and the first example of a coordinated alkoxytrifluoroborate ion.

SYNTHESIS OF MIXED THIOLATE-SELENOLATE COMPLEXES
BY EXCHANGE REACTIONS OF TETRATHIOLATOMETALLATES(II)
WITH DIPHENYLDISELENIDE

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University of Tasmania,
GPO box 252C, Hobart, Tasmania 7001

Synthetic routes to metal selenolates are often difficult due to the extreme air oxidisability of selenol reagents.

Mixed ligand complexes $(\text{Me}_4\text{N})_2[\text{M}^{\text{II}}(\text{SPh})_2(\text{SePh})_2]$ $\text{M} = \text{Zn}, \text{Cd}$ and $(\text{Me}_4\text{N})_2[\text{Hg}(\text{SPh})(\text{SePh})_3]$ have been prepared in good yield by reaction of the tetrathiolatometallate(II) precursors with diphenyldiselenide in acetonitrile.

The composition of the products is consistent with reduction of diselenide by labile benzenethiolate, with the degree of selenolate substitution determined by the relative affinity of the metal ion for sulfur or selenium donors.

METHYLMERCURY(II) COMPLEXATION BY IMIDAZOLIDINE- AND
TETRAHYDOPYRIMIDINE-2-THIONES and -SELONES

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B.W. SKELTON and A.H. WHITE,
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University of Western Australia, Nedlands, W.A. 6009

Complexation of MeHg(II) by several imidazolidine- and 2(1H)-tetrahydropyrimidine thiones and selones has been studied in solution and in the solid state.

Aqueous formation constants (β_{MLH}) have been determined by micro-computer-controlled potentiometric titration.¹ Analysis using the ESTA suite of programs² indicates that the selones form $MeHgL^+$ complexes ($\log \beta_{110} = 8.2-9.6$) which are more stable than the analogous thione complexes by about one log K unit. Except for N,N'-disubstituted ligands, $(MeHg)_2LH_{-1}$ complexes are also present ($\log \beta_{21-1} = 6.0-6.7$ for selones), even under 1:1 conditions.

$[MeHgL]NO_3$ complexes have been isolated for many of the ligands and characterised by vibrational spectroscopy. Mercury-chalcogen vibrations in the regions $220-310\text{ cm}^{-1}$ (X=S) and $160-240\text{ cm}^{-1}$ (X=Se) are consistent with near linear C-Hg-X geometry.

The structures of the isomorphous pair of complexes $[MeHgL]NO_3$ (L=2(1H)-tetrahydropyrimidine thione and selone) show linear C-Hg-X coordination. The Hg-Se bondlength (247.8(3)pm) is shorter than expected by comparison of sulfur and selenium covalent radii, consistent with the stronger Hg-Se binding indicated by formation constant and 1H NMR studies.

1. A.P. Arnold, S.D. Daignault and D.L. Rabenstein, Anal. Chem., **57**, 1112-6 (1985)
2. P.M. May, K. Murray and D.R. Williams, Talanta, **32**, 483-9 (1985)

INTEGRATED MULTINUCLEAR NMR STUDY OF OXO, SULFIDO AND SELENIDO
COMPOUNDS OF MOLYBDENUM AND TUNGSTEN

by Trevor D. Bailey, Michael Kony, Robert T.C. Brownlee
and Anthony G. Wedd

Department of Chemistry, La Trobe University

We are interested in the chemistry of the title compounds because of their involvement in biological and industrial catalysts. The relevant NMR-active nuclei (^{17}O , ^{33}S , ^{77}Se , $^{95,97}\text{Mo}$, ^{183}W) are "difficult" for one or more of the following reasons:- (a) low natural abundance, (b) low frequency resonance, (c) inherent insensitivity, (d) quadrupolar (causing broad lines). NMR of the metal nuclei in these compounds is developing satisfactorily².

The quadrupolar nuclei (^{17}O , ^{33}S , $^{95,97}\text{Mo}$) have linewidths, $W_{\frac{1}{2}}$, determined by:-

$$W_{\frac{1}{2}} = (\pi T_{2q})^{-1} = (\pi T_{1q})^{-1} = k \cdot \chi^2 \cdot \tau_c$$

If an estimate of the correlation time, τ_c , is available, then quadrupole coupling constants, χ , can be estimated and used as probes of electronic environment and stereochemistry. Correlation times may be estimated using the non-quadrupolar nuclei (^{77}Se , ^{183}W) by measurement of relaxation times as functions of magnetic field strength or temperature to isolate the contributions from the chemical shift anisotropy or spin rotation relaxation mechanisms. This approach was successful for $[\text{Mo}(\text{CO})_6]^{2a}$ and $[\text{Mo}_2(\text{O}_2\text{CR})_4]^{2b}$. Extensions to the $[\text{MO}_{4-n}\text{X}_n]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}$; $n = 0-4$) system and more complex (and interesting) species will be described.

1. M. Minelli, J.H. Enemark, R.T.C. Brownlee, M.J. O'Connor and A.G. Wedd, Coord. Chem. Rev., in press.
2. R.T.C. Brownlee, M.J. O'Connor, B.P. Shehan, M. Kony and A.G. Wedd, J. Mag. Res., 1985, (a) 61, 22; (b) 63, 343.

CHEMISTRY OF TECHNETIUM NITRIDO COMPOUNDS:
APPLICATIONS FOR NUCLEAR MEDICINE

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Technetium-99m ($t_{1/2} = 6$ hr) complexes are widely used as functional and imaging agents in nuclear medicine. Chemical studies using "carrier-free" technetium-99m are, however, not practical due to the very low molar concentrations of this radionuclide. We have performed studies by the use of the long-lived technetium-99 nuclide ($t_{1/2} = 2.12 \times 10^5$ years) which allows complexes to be isolated, characterized and studied by conventional chemical and spectroscopic methods.

The air-stable complex salts $R[TcNCl_4]$ and $R[TcNBr_4]$ [$R = AsPh_4^+$ or $N(n-Bn)_4^+$] have been prepared by the reaction of NH_4TcO_4 with NaN_3 in the presence of conc. HCl or HBr followed by precipitation with the large organic cations. Addition of CsCl to a solution of $TcNCl_4^-$ in conc. HCl results in the formation of the six-coordinate $Cs_2[TcNCl_5]$. The chloro ligands of $TcNCl_4^-$ are labile and this anion provides a convenient route to $Tc \equiv N$ complexes. Thus, reaction of the orange $AsPh_4[TcNCl_4]$ with LiBr in acetone rapidly gives the deep-blue $AsPh_4[TcNBr_4]$. The $Tc^{VI}NCl_4^-$ anion is an oxidizing agent and reaction with the reducing ligands S_2CNet_2 , PPh_3 , NCS^- , thiooxine, and thiourea results in the formation of $[TcN(S_2CNet_2)_2]$, $[TcNCl_2(PPh_3)_2]$, $[TcN(NCS)_4]^{2-}$, $[TcN(thiooxine)_2]$ and $[TcN(thiourea)_4Cl]Cl$ respectively, all of which contain the $Tc^V \equiv N$ core.

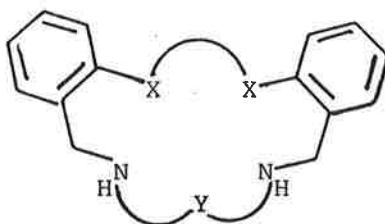
The $Tc \equiv N$ bond is surprisingly stable to acid or aqueous hydrolysis, a fact which enables the formation of ^{99m}TcN -radiopharmaceuticals. The properties of radiopharmaceuticals prepared from $^{99m}TcNCl_4^-$ have been shown to be different to those prepared, using the same ligand, by conventional reduction methods. Monoclonal antibodies labelled by the use of $^{99m}TcNCl_4^-$ have been shown to retain their specificity after labelling and to localize effectively in vivo in mouse tumours.

CALORIMETRIC AND NMR STUDIES OF THE INTERACTION OF Ag(I) WITH MIXED-DONOR MACROCYCLES

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Department of Chemistry and Biochemistry, James Cook University of North Queensland and School of Chemistry, University of New South Wales

As part of an overall investigation of the use of mixed-donor macrocycles for metal-ion discrimination, we have studied the interaction of Ag(I) with a range of macrocycles of general type (1). The effect of systematic variation of the



X = O, S

Y = O, NH, S

(1)

donor pattern within this ligand framework on the solution chemistry and thermochemistry of the corresponding Ag(I) species has been investigated. For example, complementary calorimetric and nuclear magnetic resonance studies in acetonitrile (and its deuterated derivative) have been used to investigate the nature of the equilibria present as the Ag(I):macrocycle ratio is varied.

The effects of macrocycle structure on the heats of formation and on the stepwise equilibrium constants for particular silver complexes will be presented.

A Synthetic Route to Encapsulated Ru Compounds: Properties of the Ru(sar)^{2+/3+} Ions

Paul Bernhard and Alan M. Sargeson

Research School of Chemistry, Australian National University, Canberra

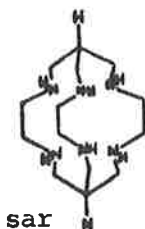
The relatively labile Ru(DMF)₆²⁺ complex (DMF: N,N-dimethylformamide) was found to be a useful starting complex in the synthesis of encapsulated Ru complexes.

By refluxing a dry ethanolic solution of Ru(DMF)₆(X)₂ (X: CF₃SO₃⁻, to⁻), prepared in 90 % yield from Ru(H₂O)₆(X)₂, and of sar (1) in a strictly O₂ - free atmosphere for 2 days Ru(sar)(X)₂ was obtained in 60 - 70 % yield.

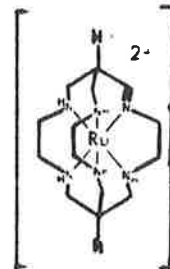
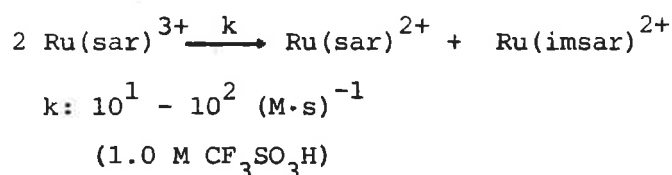
Ru(sar)(CF₃SO₃)₃ was isolated from dry acetonitrile after electrochemical or chemical oxidation of Ru(sar)²⁺. From the rates of oxidation of Ru(sar)²⁺ by the complexes (NH₃)₅RuL³⁺ (L: pyridine, nicotinamide, isonicotinamide) a value of ~10⁵ (M.s)⁻¹ (25.0 °C, 1.0 M CF₃SO₃H) for the Ru(sar)^{3+/2+} self exchange was obtained.

Even in strongly acidic aqueous solutions, however, Ru(sar)³⁺ appeared to be stable only on the voltammetric timescale (E⁰: 0.29 V vs NHE) and disproportionated (2):

(1)



(2)



The Ru(II) monoimine complex exhibited a characteristic t_{2g}(Ru) → π*(L) charge transfer band (392 nm) and was oxidized further to give polyimine complexes.

Structural Principles for Fluorite-related Superstructures.

D.J.M. Bevan, C. Collyer and S.E. Lavton.

The Flinders University of South Australia.

The solution of the structure of the mineral tveitite - $\text{Ca}_{14}\text{Y}_5\text{F}_{43}$ (1) led to the recognition of a new structural principle (2) for anion-excess superstructures. As in all fluorite-related structures, the cation array remains as essentially unaltered f.c.c., and it is the anion arrangement which is varied. The fundamental step in this process is the conversion of X_8 anion cubes in fluorite to X_8 anion square antiprisms. More specifically, the fluorite element (M_6X_{32}) of six MX_8 cubes sharing edges to enclose an empty X_8 cube is converted to a cluster of six MX_8 square antiprisms sharing corners to enclose an empty cuboctahedron. This can be represented formally by: $\text{M}_6\text{X}_{32} + 4\text{X} \rightarrow \text{M}_6\text{X}_{36}$, and if an additional anion is accommodated at the centre of the cuboctahedron, the cluster becomes M_6X_{37} .

This cluster principle has now been used widely in new descriptions of known structures, and in constructing models of unknown structures.

For anion-deficient superstructures there is a great dearth of structural information despite the occurrence of many such phases. Only the structure of the M_7O_{12} phases (typified by UY_6O_{12}) is well known, and from it we have derived a different but closely-related cluster which may be, and we believe is, the clue to many unknown structures of this class.

Thus the way is clear to build sensible models of the structures of all the known $\text{M}_n\text{O}_{2n-2}$ ($n = 7 + m$) phases occurring in the binary systems $\text{R} + \text{O}$ ($\text{R} = \text{Ce}, \text{Pr}, \text{Tb}$), and to use atom positions calculated from models as the starting point for structural refinement.

So, for both anion excess and anion-deficient phases there is in all these models a common theme, viz., the transformation of fluorite cubes, either empty or filled, to square antiprisms, or part thereof, and this establishes for the first time a non-trivial structural link between the two types.

Examples of these models will be displayed.

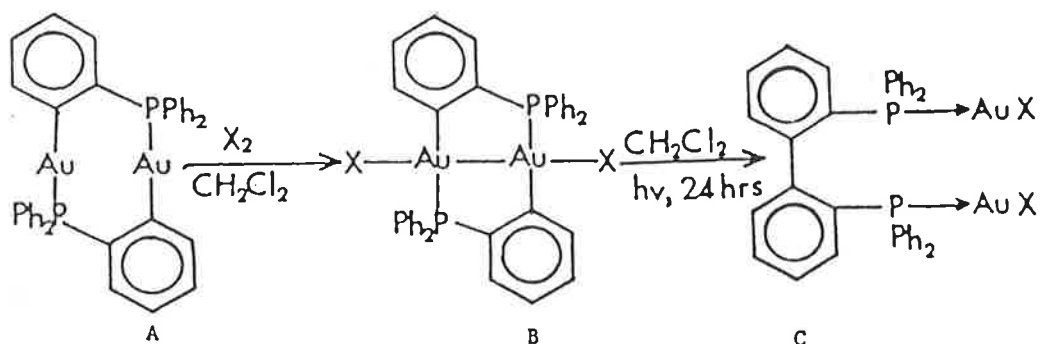
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DINUCLEAR GOLD COMPLEXES BRIDGING THROUGH C AND P OR As: A NOVEL REARRANGEMENT AT DIMETALLIC CENTRE.

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A series of novel dinuclear gold(I) complexes bridging through ortho-metallated-tertiary phosphine or arsine has been made from $\text{AuCl}(\text{PEt}_3)$ and $\text{O-LiC}_6\text{H}_4\text{ER}_2$ ($\text{E}=\text{P}$, $\text{R}=\text{Ph}$ or Et ; $\text{E}=\text{As}$, $\text{R}=\text{Me}$). X-ray analysis of $[\{\text{Au}(\text{O-C}_6\text{H}_4\text{PPh}_2)\}_2]$. (A) shows the gold atoms to be only 2.86 Å apart. The complex undergoes oxidative addition with halogens and with CH_3I to produce Au(II)-Au(II) complexes (B). The Au-Au distance in (B) ($\text{X}=\text{I}$) is 2.60 Å. These complexes rearrange in solution with coupling of the cyclometallated rings to produce (C)



$\text{X} = \text{Cl}, \text{Br}$ or I

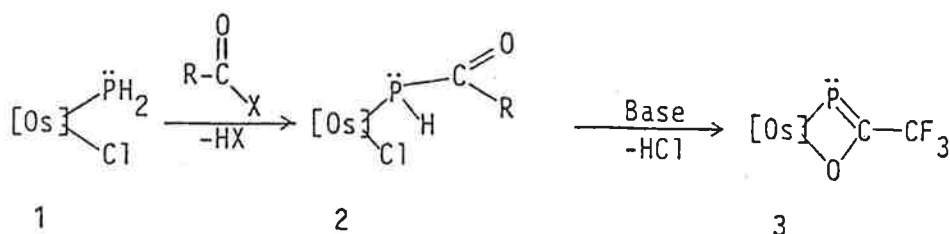
The presence of the biphenyl-based ligand in (C) has been confirmed by X-ray analysis of the bromo-complex.

A P-Metallated Phospha-alkene Complex with Terminal Phosphinidene Character

D. Scott Bohle, C.E.F. Rickard and W.R. Roper.

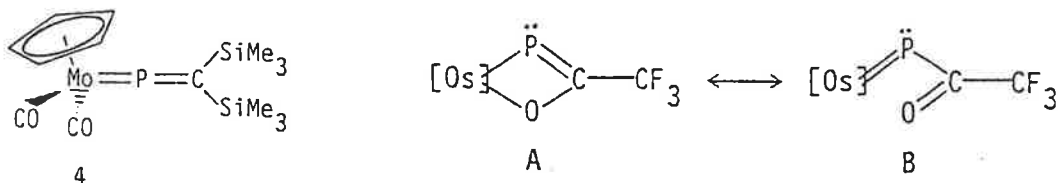
Department of Chemistry, The University of Auckland, Private Bag, Auckland, New Zealand.

A synthetically versatile terminal phosphido-complex $\text{Os}(\text{PH}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$, 1, is prepared in three high yield steps from phosphine and $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$.¹ Particularly useful acyl phosphido-complexes, $\text{Os}[\text{PH}\{\text{C}(\text{O})\text{R}\}]\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$, 2, are derived from 1 by treating it with acid halides or anhydrides.



$[\text{Os}] = \text{Os}(\text{CO})_2(\text{PPh}_3)_2$; $\text{X} = \text{Cl}^-$, CF_3CO_2^- ; $\text{R} = \text{CF}_3$, Ph , CO_2Et .

The presence of an acyl substituent increases the acidity of the phosphorus bound hydrogen to the extent that bases such as DBU or sodium hydride readily abstract HCl from 2 to give $\text{Os}[\text{P}=\text{C}(\text{O})\text{CF}_3](\text{CO})_2(\text{PPh}_3)_2$, 3. A bent geometry for the η^2 -phospha-alkene ligand in 2 [$\text{Os}-\text{P}-\text{C} = 73.6(8)^\circ$] stands in marked contrast with another complex, 4, which has a linear $\text{Mo}-\text{P}-\text{C}$ arrangement.² However, the long $\text{Os}-\text{O}$ bond length [$2.226(1)\text{\AA}$] and short $\text{Os}-\text{P}$ and $\text{C}-\text{O}$ bond lengths [$2.482(6)$ and $1.246(27)$ respectively] suggest that the bonding in 3 is best represented by A and B. Indeed the reaction of 3 with PPh_3AuCl or R_4NAuI_2 results in overall addition of AuX across the $\text{Os}=\text{P}$ bond as in B.



¹D.S. Bohle, T.C. Jones, C.E.F. Rickard and W.R. Roper, J.C.S. Chem. Commun. 1984, 865.

²A.H. Cowley, N.C. Norman and S. Quashie, J.Am.Chem.Soc., 1984, 106, 5007.

The Electronic Structure and Spin State of the Bis(tetrathiomolybdate)iron trianion, $[\text{Fe}(\text{MoS}_4)_2]^{3-}$.

By Graham A. Bowmaker, Peter D.W. Boyd and Richard J. Sorrenson,
Chemistry Department, University of Auckland, Auckland, New Zealand,
Christopher A. Reed, Department of Chemistry, University of Southern
California,
and John W. McDonald, Battelle-Kettering Laboratory, Ohio.

The tetrathiomolybdate anion MoS_4^{2-} when combined with iron gives a variety of multimetallic clusters. The bis(tetrathiomolybdate)iron trianion, $[\text{Fe}(\text{MoS}_4)_2]^{3-}$, was reported simultaneously by Coucouvanis¹ and by McDonald² in 1980. The complex consists of an iron atom tetrahedrally coordinated by two bidentate MoS_4^{2-} groups. The esr and magnetic moment have been interpreted in terms of a $S=3/2$ ground state. Three formulations of the $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ ion that lead to an $S=3/2$ ground state are possible: a low-spin iron(III) ($S=\frac{1}{2}$) atom ferromagnetically coupled to two molybdenum(V) $S=\frac{1}{2}$ centers; a high-spin iron(III) ($S=5/2$) atom antiferromagnetically coupled to two molybdenum(V) $S=\frac{1}{2}$ centers; and an iron(I) $S=3/2$ atom bound by two diamagnetic MoS_4^{2-} ligands. The first of these is extremely unlikely since tetrahedral iron(III) complexes are not expected to be low spin. The second formulation is favoured from Mössbauer isomer shifts arguments² and esr spectroscopy.³

The magnetic susceptibility (1.7–300K) and low temperature (1.7–30K) magnetisation (1–4T) of the bis(tetrathiomolybdate)iron trianion in polycrystalline $[\text{Et}_4\text{N}]_3[\text{Fe}(\text{MoS}_4)_2]$ have been measured. The temperature and field dependence of the magnetisation unequivocally demonstrate the $S=3/2$ orbital singlet ground state with a substantial zero field splitting, $g = 1.985$, $D = +4.4 \text{ cm}^{-1}$. Scattered wave-SCF-X α calculations of the electronic structure of the $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ anion (D_{2d} symmetry) suggest that this spin state arises from occupancy of the iron d orbitals by seven electrons leading to a ground state electronic configuration $(z^2)^2 (xy)^2 (x^2-y^2)^1 (xz,yz)^2$. This leads to the reformulation of $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ as an iron(I) complex coordinated by two Mo(VI)S_4^{2-} anions. The resulting charge distribution, however, is close to that of analogous d^6 iron(II) complexes. The extra charge in the trianion is principally delocalised over the tetrathiomolybdate anions. This is also observed in the analogous cobalt complexes $[\text{Co}(\text{WS}_4)_2]^{n-}$ ($n=2,3,4$). Calculation of the Mössbauer quadrupole splitting agrees well with the experimentally reported value. Contributions to the electric field gradient from both iron p and d electrons are found to be of similar magnitude. These calculations also suggest an explanation for why the iron isomer shifts in $[\text{Fe}(\text{WS}_4)_2]^{2-/3-}$ are almost identical but their quadrupole splittings are markedly different.

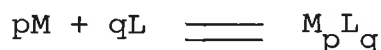
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THE PREDICTION OF THE FORMATION CONSTANTS OF METAL ION COMPLEXES

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Australian Atomic Energy Commission,
Private Mail Bag, Sutherland, 2232

The formation of a metal ion complex as given by the (hypothetical) reaction (charges are ignored)



have an associated stoichiometric formation constant defined as

$$\beta_{pq} = \frac{[M_p L_q]}{[M]^p [L]^q}$$

We have previously shown¹ that this formation constant, for hydroxo-metal ion complexes, can be predicted, in almost all instances, by using the following equation;

$$\log \beta_{pq} = [q(Int_1) + (p-1)Int_2] + [q(Slp_1) + (p-1)Slp_2] [g_1 (z/r^2 + g_2)]$$

In the equation, z is the ionic charge and r the ionic radius of the metal ion, Int_1 and Slp_1 , and Int_2 and Slp_2 , are the least squares intercept and slope values of linear equations for the (1,1) species and the polymeric (p,q) species, respectively, and g_1 and g_2 are functions of only the charge and electronic structure of the metal ion.

We have now extended this concept so that the formation constant of any metal ion complex, mononuclear or polynuclear, unidentate or multidentate may be predicted.

Reference

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Comparisons of the Shapes of First and Second Row Triatomic Species

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Chicago, Illinois 60637, U.S.A., and

²Department of Inorganic Chemistry,
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There are extensive differences in structural chemistry between compounds of the first and subsequent rows of the periodic table. We have undertaken a theoretical study of the simplest possible systems in which such differences can arise. We present results for Si_3 , P_3^+ , P_3^- , S_3 , Cl_3^+ and Cl_3^- , and their first-row counterparts. Our ab initio techniques usually predict molecular structural parameters to within 1-2%. Final calculated energies include valence electron correlation.

Our most striking results involve P_3^+ and P_3^- . Although N_3^+ has a linear triplet ground state, we predict P_3^+ to be most stable as a triangular (D_{3h}) singlet. We have computed force constants and vibrational frequencies to assist experimental attempts to characterize P_3^+ ; synthetic work directed towards its preparation is underway in Melbourne (Professor T.A. O'Donnell). While N_3^- is a rigid linear singlet, there are three electronic states of P_3^- all close in energy, a linear singlet, a sharply bent singlet (bond angle 72°) and a triangular (D_{3h}) triplet.

The contrasting shapes of first and second row systems are discussed, stressing the relative importance of σ and π bonding and the differing participation of valence s and p orbitals.

DEVELOPMENT AND APPLICATION OF A VERSATILE
COMPUTER BASED DATA ACQUISITION SYSTEM
FOR USE IN THE LABORATORY.

A. Campisi, M.R. Grace and P.A. Tregloan.

Department of Inorganic Chemistry,
University of Melbourne.

We have been involved in the development and use of a number of laboratory computer systems. The aim of this work has been to provide a flexible facility, readily adaptable to a wide range of experimental and instrumental situations.

In developing this facility, we have made use of :

- (i) a DEC PDP/11 minicomputer system using commercially available interface modules. The operation of these modules for a particular experiment is achieved through a special set of additional machine code subroutines, callable from a BASIC program.
- (ii) a Motorola M6800 microcomputer system. Based on our experience with the earlier DEC system, the computer and experiment interfaces were designed and developed in our Department, together with the necessary control software.
- (iii) Apple Macintosh personal computers. These units are at present being used primarily for the analysis of data transmitted from either (i) or (ii); the procedures make particular use of the powerful graphics capability of the Macintosh. It is planned that these units will be used interactively with systems (i) and (ii), or with specifically built instrument interfaces, for experiment control and data collection.

The specification of each of these systems and their application to a range of instruments, including spectrophotometric, titrimetric and stopped-flow kinetic equipment will be reported.

Olefin Oligomerization and Isomerization Catalysts and the Effects
of Chelating Ligands on Activity and Product Distribution.

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CSIRO, Division of Materials Science,
Locked Bag 33, Normanby Road,
Clayton, Victoria 3168

Light olefins may be generated by several established routes; catalytic cracking, or from natural gas via synthesis gas conversion or via the intermediate production of methanol. Further processing of these olefins yield transport fuels or important feeds for specialty chemicals. Soluble nickel based organometallic catalysts have received extensive commercialization in both these areas.

A nickel (II) SacSac (SacSac = dithioacetylacetonate) based catalyst system, for olefin oligomerization and isomerization developed at the CSIRO Division of Materials Science has been the subject of several patents and publications in the open literature. This presentation concerns further developments in the catalyst system which broaden its potential for commercialization.

Further modifications to catalyst activity and product distribution may be effected by the incorporation of chelating phosphine ligands in the CSIRO catalysts. Methods of preparing the chelate containing complexes will be briefly mentioned. Catalyst testing and important changes in the product distribution will be discussed.

CONVERSION OF LIGHT OLEFINS WITH HIGHLY ACTIVE
NICKEL CATALYSTS. (I)
CATALYTIC ASPECTS OF HOMOGENEOUS SYSTEMS

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Australia.

The reactions of light olefins derived from natural gas conversion and synthesis gas chemistry lead to a number of industrially important products. In particular, the oligomerization and co-oligomerization of ethylene, propylene and butene yield products useful as octane extenders in unleaded fuels and as intermediates in plasticizer synthesis. Although catalytic olefin oligomerization is well established commercially, the available technologies variously suffer from low activity, poor conversions, relatively severe operating conditions, poor selectivity and short catalyst lifetimes. A significant drawback in both applications areas is the production of large amounts of undesirable heavily branched products.

The CSIRO Division of Materials Science has developed a novel catalyst system based on a nickel organometallic compound in combination with a catalyst activator. By contrast with the available technologies, the new catalyst system is highly active at ambient temperatures and pressures, can be made up to 99% selective for dimerization, has a long operating lifetime and a high specificity for industrially desirable products. The nickel precursors can be synthesized in high yields as air stable crystalline solids from cheap, abundant starting materials and are extremely soluble in hydrocarbon media.

The catalyst system will be described and discussed with particular emphasis on the facility with which operational parameters can be varied and controlled by simple modifications to substituents of a ligands surrounding the catalytically active nickel centre.

BENZENE-1,2-DITHIOLATO COMPLEXES OF TECHNETIUM

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^bAustralian Radiation Laboratory,
Lower Plenty Rd, Yallambie, Victoria 3085.

Technetium in its metastable form (^{99m}Tc) has found widespread use as an ideal imaging agent ($t_{1/2}$ 6h, γ 140 keV) in diagnostic nuclear medicine. However, because of the extremely low molar concentrations involved ($\text{ca } 10^{-8} \text{ mol dm}^{-3}$) the chemistry of technetium is poorly understood. In recent years this problem has been largely overcome by the use of long-lived technetium - 99 ($t_{1/2}$ $2.12 \times 10^5 \text{ y}$), which makes it possible to isolate substantial amounts of technetium compounds for characterization by conventional chemical and spectroscopic techniques. The reaction of benzene-1,2-dithiol with $(\text{C}_6\text{H}_5)_4\text{AsTcOCl}_4$ and with NH_4TcO_4 in aqueous alcohol yielded crystals of $(\text{C}_6\text{H}_5)_4\text{AsTcO}(\text{C}_6\text{H}_4\text{S}_2)_2$ from acetonitrile and crystals of $\text{Tc}_2(\text{C}_6\text{H}_4\text{S}_2)_4 \cdot \text{CHCl}_3$ from chloroform respectively. The structures of these compounds have been determined by single-crystal X-ray diffraction methods.

The compound $(\text{C}_6\text{H}_5)_4\text{AsTcO}(\text{C}_6\text{H}_4\text{S}_2)_2$ crystallizes in the monoclinic space group Cc with $a = 12.652(1)$, $b = 15.783(1)$, $c = 16.622(1) \text{ \AA}$, $\beta = 93.03(1)^\circ$ with $Z = 4$. Refinement with data measured with Cu K α radiation converged at $R = 0.030$ for 2828 observed terms. The structure consists of $[\text{TcO}(\text{C}_6\text{H}_4\text{S}_2)_2]^-$ anions and $[\text{Ph}_4\text{As}]^+$ cations. The technetium(V) atom is five-coordinate, with the four sulphur atoms in equatorial positions and the oxo ligand in the apical position, to give a distorted square pyramidal environment. The distortion is a consequence of the strong *trans* effect exerted by the oxo ligand which causes the Tc atom to lie $0.732(1) \text{ \AA}$ above the plane of the four S atoms. The structure is typical of other complexes containing the MO_5 core ($M = \text{Mo, Re, Tc, V}$).

Triclinic crystals of $\text{Tc}_2(\text{C}_6\text{H}_4\text{S}_2)_4 \cdot \text{CHCl}_3$ belong to the space group $P\bar{1}$ with $a = 8.534(1)$, $b = 8.842(2)$, $c = 11.192(3) \text{ \AA}$, $\alpha = 107.02(2)$, $\beta = 98.13(1)$, $\gamma = 100.60(2)^\circ$ and $Z = 1$. Refinement with 1524 observed data measured with Cu K α radiation converged at $R = 0.082$. The binuclear technetium(IV) complex has i symmetry and a novel trigonal-prismatic geometry. The Tc atoms are seven-coordinate with six sulphurs around each which define two trigonal prisms with a shared quadrilateral face. The Tc - Tc bond (bond length $2.591(3) \text{ \AA}$) passes through the centre of the shared face so that the geometry can be described in terms of capped trigonal prisms. The chloroform molecules are disordered over inversion centres, and have been included in the structural model constrained to the generally accepted geometry.

DISTRIBUTION OF ACTINIDES AND OTHER RADIOACTIVE METALS
IN THE MILLING PROCESS OF URANIUM ORE
- THE ENVIRONMENTAL CONSEQUENCES.

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Yallambie, Victoria, Australia 3085.

An important aspect of the assessment of the environmental impact of uranium mining and milling is an understanding of the chemistry of radioactive metals mobilized during the milling of the uranium ore and, over a long period of time, from tailings material.

Uranium is extracted from ore with an efficiency of 95% or more by a sulphuric acid leach process. During the mill circuit a significant quantity of Th-230, a toxic, long-lived radioactive daughter of uranium (U-238), is also dissolved. The solubility of other environmentally-important radioactive metals, Ra-226, Pb-210 and Ac-227, is dependent on both the pH at the particular stage of the process and on the sulphate concentration in the liquid tailings.

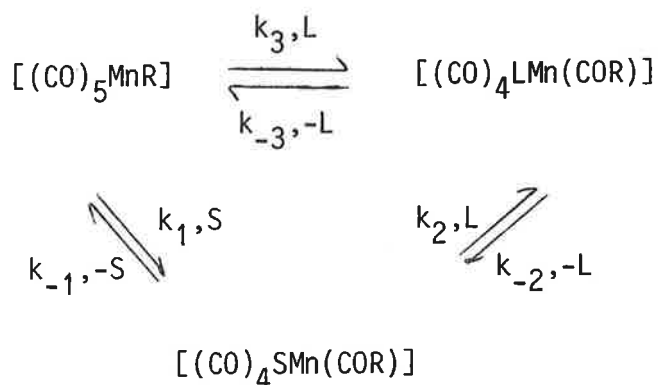
The long-term release rates of long-lived radioactive metals from tailings are being studied and results indicate that solubility factors rather than kinetics control the leaching behaviour of tailings. Radium (Ra-226) appears to be the most mobile species in terms of the long-term release of radioactivity from rehabilitated tailings. The most likely chemical state of soluble radium is a neutral inorganic complex. Our investigations have shown that complexes of this type will become readily adsorbed on to colloids and particulate matter in natural waters.

SYNTHETIC, STRUCTURAL AND MECHANISTIC STUDIES OF CO INSERTION

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Department of Chemistry, University of Queensland, Brisbane, 4067

The steric and electronic effects of the substituted benzyl group, R, the tertiary phosphine, L, and the solvent, S, in the multi-stage reaction shown in the scheme



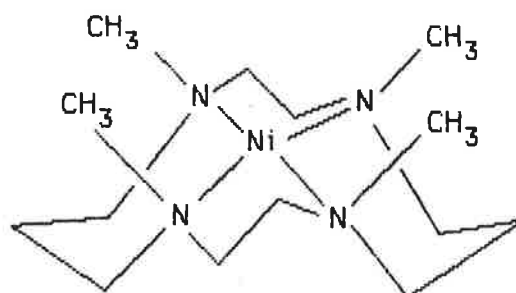
are presented. In polar solvents (the k_1 , k_2 path), higher reactivity is observed above a threshold level of steric influence of substituents in the ortho- position of the benzyl group. The steric effect of the phosphine is predominant in the k_2 path but its electronic nature is the major influence in the "direct" k_3 pathway in non-polar solvents. Correlation of reactivity with structural features (e.g. lengthening of the Mn-C bond) of strategically substituted compounds will be attempted. Although the $[(\text{CO})_5\text{MnR}]$ compounds, the phosphine-substituted acyls, $[(\text{CO})_4\text{LMn}(\text{CoR})]$, and the decarbonylation products $[(\text{CO})_4\text{LMnR}]$ are highly unsymmetrical molecules, reasonably sharp ^{55}Mn NMR resonances have been observed; trends in chemical shifts and $J(^{55}\text{Mn}-^{31}\text{P})$ are examined.

STRUCTURAL AND EQUILIBRIUM STUDIES OF
R,S,R,S- (1,4,8,11-TETRAMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECANE)
NICKEL(II) PERCHLORATE IN ACETONITRILE.

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Dept of Inorganic Chemistry, University of Melbourne.
Parkville, Victoria, 3052. AUSTRALIA.

An investigation of the spin-state equilibrium involving the R,S,R,S- nickel(II) complex of the macrocyclic ligand 1,4,8,11- tetramethyl 1,4,8,11- tetraazacyclotetradecane (commonly called tetramethylcyclam or tmc) in acetonitrile has been conducted. This study confirms that the title complex exists as an equilibrium mixture of diamagnetic four coordinate and paramagnetic five coordinate species in this solvent.



The R,S,R,S Isomer of $[\text{Ni}(\text{tmc})]^{2+}$

Single crystal X-ray diffraction studies of the complexes involved in the above equilibrium have also been undertaken [1,2]. The unsolvated macrocyclic centre adopts a distorted square planar arrangement of nitrogen atoms around the nickel centre. The solvated nickel centre assumes a distorted square pyramidal geometry with the solvent molecule occupying the apical position and the nickel centre displaced from the N_4 plane by 0.34 Å. The Ni-N bonds lengths increase from an average of 1.96 to 2.14 Å with the expansion of the coordination sphere of the Ni atom. Both the four and five coordinate cations possess the R,S,R,S ligand conformation shown in the Figure.

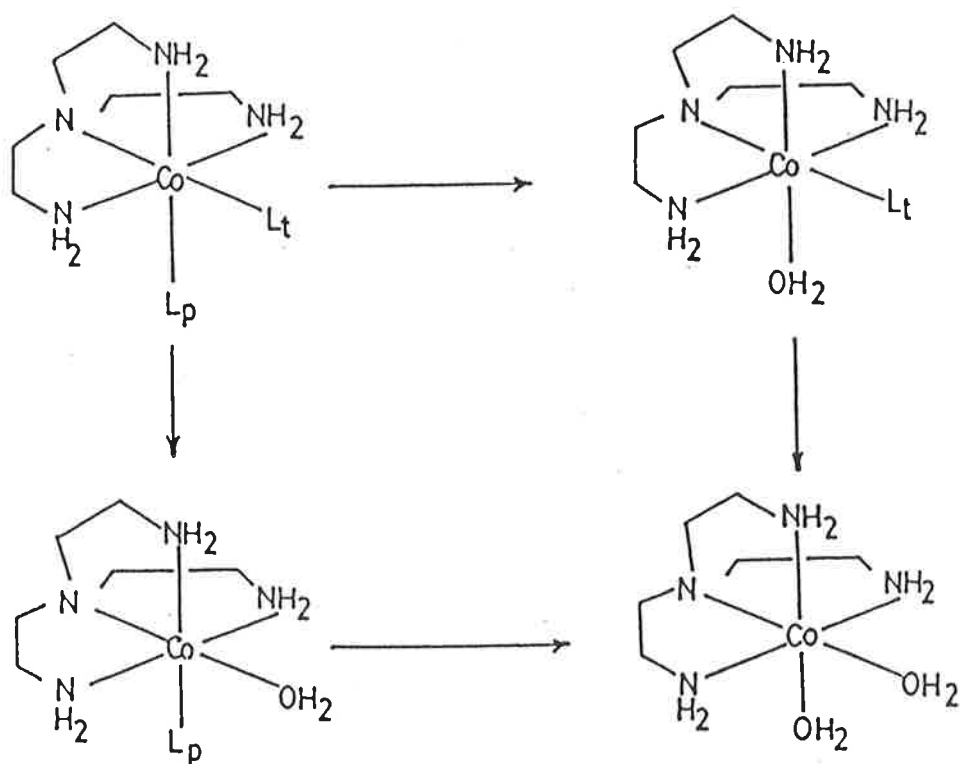
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SYNTHESES, CHARACTERISATION AND HYDROLYSES OF TRENBI(SOLVENT)COBALT(III) COMPLEXES

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b. Department of Chemistry, University of Newcastle, NSW

The stereochemical rigidity imposed by the tren ligand system in trenbis(solvent)cobalt(III) complexes renders the two solvent ligands (L_t and L_p) inequivalent, as was clearly seen by the appearance of ^ptwo sets of signals in the ¹H NMR spectrum.



Spontaneous hydrolysis in 0.1 M acid gave rise to two separate kinetic events (k_1 and k_2) which were both composite rate constants derived from approximately equal ligand loss from the two unique sites. The ratios k_1/k_2 (50°) were in the range 5-10 for the neutral ligands studied, which is considerably smaller than that seen for the dichloro (470) and dibromo (2660) complexes. At higher pH's, both k_1 and k_2 had base catalysed counterparts, the latter of which was equated with a a_2^{2+} conjugate base mechanism involving $trenCo(solvent)OH^{2+}$.

The preparations of the complexes, via the triflate, and the kinetics and mechanisms of the hydrolyses will be presented.

EFFECTS OF Zn/Cd AND S/Se SUBSTITUTION IN THE TETRA-ADAMANTANOID CAGE
 $[S_4Cd_{10}(SPh)_{16}]^{4-}$, IN RELATION TO HETEROMETAL METALLOTHIONEINS.

Ian Dance

School of Chemistry, University of New South Wales, NSW 2033.

^{113}Cd NMR spectra of various mixtures of the cage compounds $[M_4(SR)_{10}]^{2-}$ (1) and $[E_4M_{10}(SR)_{16}]^{4-}$ (2) ($M = Zn, Cd$; $E = S, Se$) reveal the exchange reactions of M and E which occur within the different structural elements of (2), namely the triply-bridging chalcogenide ligands E , the inner metal atoms M^i , and the outer metal atoms M^o . At laboratory temperature the exchange timescales range from days (E) through hours (M^i) to seconds (M^o and SPh). Metal exchange does not always follow random statistics, with biases towards equilibrium association of the same metal. The M -substituted and E -substituted products, with lower symmetry and more informative spectra than the high symmetry precursors, reveal the mutual influences of the various structural elements on the Cd chemical shifts: $S \rightarrow Se$ substitution causes changes ($\Delta\delta Cd$) of $-37ppm$ at one bond, $-3ppm$ and $-1.5ppm$ at three bonds, and $+1ppm$ five bonds distant; $Cd \rightarrow Zn$ substitution causes δCd to change by $+13ppm$ and $+5ppm$ at a connection of two bonds and by $-3ppm$ over four bonds. These effects of adjacent $Cd \rightarrow Zn$ substitution on δCd provide well-defined models in support of the hypothesis of similar effects in the Cd NMR spectra of mixed Zn/Cd metallothionein proteins.

LARGE MOLECULAR FRAGMENTS OF METAL CHALCOGENIDE LATTICES?

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$[M_4(SR)_{10}]^{2-}$ (1) and $[E_4M_{10}(SR)_{16}]^{4-}$ (2) ($M = Zn, Cd$; $E = S, Se$) are known molecular species, with adamantanoid and tetra-adamantanoid cage structures. In both (1) and (2) the cores of metal and chalcogenide atoms are structurally congruent with the cubic (sphalerite) metal chalcogenide ME , and the overall shape of the aggregate is tetrahedral. By expansion of this pattern we can conceive of an unlimited series of super-tetrahedral molecules $[E_eM_x(SR)_y]^{z-}$, all terminated with thiolate ligands only at the edges and vertices, and all structurally congruent with sphalerite. The general formulation of molecules in this series will be described, together with their sizes and calculated surface charge densities, and relationships with colloidal CdS .

Reactions which could lead to molecules in this series will be evaluated, as will the feasibility of identification of them in solution.

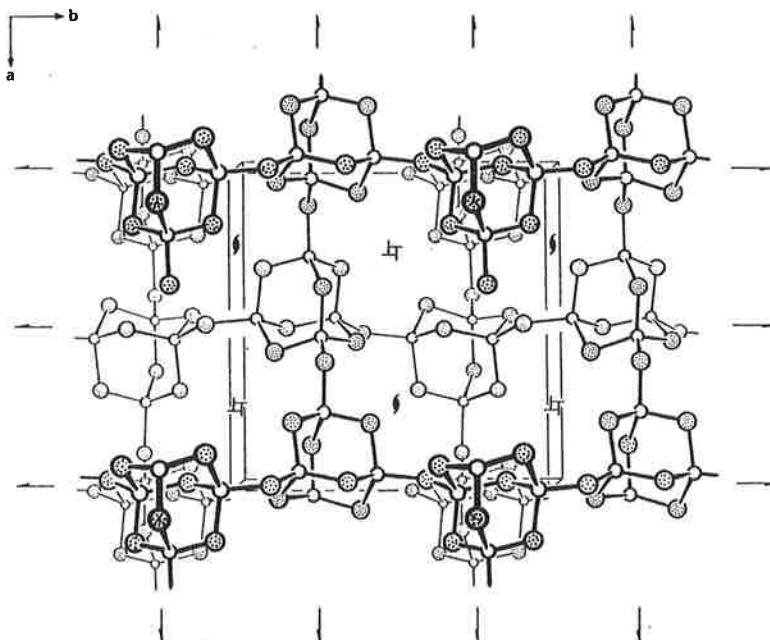
These super-tetrahedral molecules would be characterised by planar faces (mimicking the surface of the metal chalcogenide) and by sharp edges and vertices. The principles of the structural mechanisms which permit chemically acceptable termination of metal chalcogenide fragments by thiolate ligands will be examined, in search for alternative, globular, aggregate structures.

THE THREE-DimensionALLY NON-MOLECULAR POLY-ADAMANTANOID STRUCTURE OF Cd(SPh)₂

Ian Dance, Don Craig, and Robert Garbutt

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Crystalline Cd(SPh)₂ is in fact $\infty\{(\mu\text{-SPh})_6\text{Cd}_4(\mu\text{-SPh})_{4/2}\}$, in which adamantanoid cages are linked through all four outer vertices as shown in the diagram (phenyl groups omitted). The cages are linked along twofold screw axes parallel to a and b (space group P2₁2₁2₁), while helices of linked cages (about pseudo 4₁ axes, exact 2₁ axes) occur along the c direction. This is the first three-dimensionally non-molecular structure reported for a metal thiolate, and the first three-dimensionally non-molecular poly-adamantanoid structure. An alternative presentation of the structure of Cd(SPh)₂ derives from the conception of the Cd₄S₁₀ adamantanoid cage as a large tetrahedron: the large tetrahedra are linked in a pattern which is very similar to that of α -cristobalite, but more open in order that the phenyl groups be accommodated.



Solutions of Cd(SPh)₂ in DMF show a single broad resonance in the ¹¹³Cd NMR spectrum, narrowed by temperature reduction, at a chemical shift which is consistent with cadmium coordinated only by PhS⁻. The possibility will be considered that this spectrum is due to the tetra-adamantanoid molecule Cd₁₀(SPh)₂₀, or tetrahedro-(μ_3 -SPh)₄-octahedro-Cd₆-truncated tetrahedro-(μ -SPh)₁₂-tetrahedro-(CdSPh)₄.

Attention is drawn to the distinction between non-molecular poly-adamantanoid structures, with linked cages, and the molecular poly-adamantanoid aggregates (discussed also in an accompanying abstract) with fused cages.

THE DIGONAL, TETRAHEDRAL, AND CUBIC STEREOCHEMISTRY (DYNAMIC?) OF
HALIDE INCLUSION IN OCTA-METAL CAGES

Ian Dance, Robert Garbutt, and Don Craig

School of Chemistry, University of New South Wales, NSW 2033.

The known aggregate $\text{ICd}_8(\text{SCH}_2\text{CH}_2\text{OH})_{12}\text{I}_3$ (1) contains a distorted cube of cadmium atoms intersecting a pseudo-icosahedron of bridging sulfur atoms, centred by an I^- ion which has distant and irregular ($\text{I}-\text{Cd} = 3.1$ to 3.9\AA) cubic Cd_8 coordination. In contrast, crystalline $\text{ClCd}_8(\text{SCH}_2\text{CH}_2\text{OH})_{12}\text{Cl}_3$ (2) (space group $R\bar{3}$) contains an exactly threefold molecular aggregate, in which the Cd_8 cube has undergone contraction along a body diagonal to enable two Cd atoms to be closely bound to the central Cl^- ion at 2.69\AA : the other six Cd atoms are 3.58\AA from the central Cl. Thus in (2) two Cd atoms (each with tetrahedral coordination) are located inside triangular $(\mu-\text{S})_3$ faces of the S_{12} pseudo-icosahedron, while the other six Cd atoms lie outside such faces, and (2) can be described in concentric polyhedral notation as centro-(μ -Cl)-diagono- Cd_2 -icosahedro-(μ - $\text{SCH}_2\text{CH}_2\text{OH}$) $_{12}$ -trigonal-antiprismo- Cd_6 -triangulo- Cl_3 .

Regular tetrahedral coordination of the central halide, a stereochemistry intermediate between those of (1) and (2), occurs in centro-(μ_4 -Cl)-tetrahedro- Zn_4 -icosahedro-(μ -SPh) $_{12}$ -tetrahedro-(ZnSPh) $_4$. We shall describe also metrical details of $\text{BrCd}_8(\text{SCH}_2\text{CH}_2\text{OH})_{12}\text{Br}_3$ (3), isostructural with (2).

^{113}Cd NMR spectroscopy has been used to investigate the structures and dynamics of (1), (2) and (3) in DMF solution. Interconversions of Cd sites occur, and temperature reduction to $< 250\text{K}$ is necessary to reach the slow interconversion regime. Correlations of Cd chemical shift with Cd coordination environment in these systems are aided by the Cd NMR spectra of the tetra-adamantanoid aggregate $\text{Cd}_{10}(\text{SCH}_2\text{CH}_2\text{OH})_{16}\text{Cl}_4$ (4). The crystal structure of (4), to be described, contains a six-coordinate CdS_4O_2 site with unprecedented stereochemistry.

VANADIUM COMPLEXES WITH TRIDENTATE LIGANDS

Alex A. Diamantis, Janette M. Frederiksen, Ernst Horn, Md. Abdus Salam, Michael R. Snow and Edward R.T. Tiekink

Jordan Laboratories, Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, South Australia, 5001.

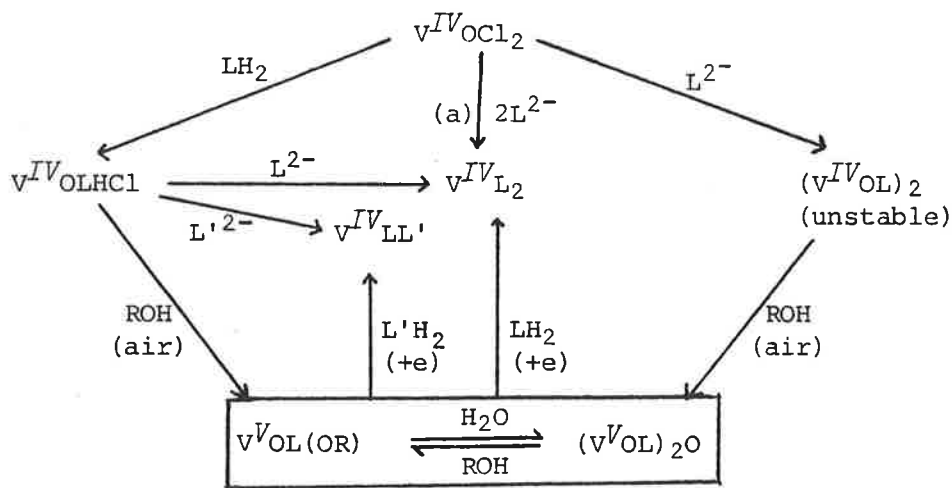
Although the chemistry of vanadium (+4) is dominated by the VO^{2+} group, certain dinegative tridentate ligands, L^{2-} , form stable six-coordinate, non-vanadyl complexes. Three types of such ligands have been developed:

- Schiff bases of aroylhydrazines with β -diketones or *o*-hydroxy aldehydes (or ketones).
- Schiff bases of *o*-aminophenols with the same carbonyl compounds.
- 2,2'-dihydroxoazoarenes.

In all cases the ligands are planar, with the donors $\text{O}^-\text{N}^-\text{O}^-$ forming a five- and a six-membered chelate rings. The complexes VL show strong LMCT bands in the visible region and characteristic e.p.r. spectra. Type (a) ligands have the V in a trigonal prismatic coordination; type (b) in an irregular octahedron.

A number of $\text{VO}(+2)$ and $\text{VO}(+3)$ complexes containing the same L^{2-} have been prepared in an attempt to elucidate the reaction mechanism of the formation of VL_2 . With type (a) ligands reaction of equimolar amounts of VO^{2+} and L^{2-} give a readily oxidisable $(\text{VOL})_2$ which in turn gives the vanadium (+5) complexes $\text{VOL}(\text{OR})$ and $(\text{VOL})_2\text{O}$ in which the vanadium has a square pyramidal coordination. The monomeric $\text{V}^{\text{IV}}\text{OLHCl}$ can be used to form mixed ligand complexes of the type VLL' .

The various preparative schemes are summarised below:



(+e) reducer, usually benzoylhydrazine

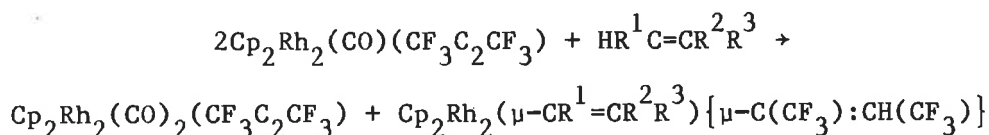
(a) also from $\text{VO}(\text{acac})_2$ and LH_2

**SUNLIGHT ASSISTED C-H BOND CLEAVAGE REACTIONS INVOLVING
OLEFINS, CYCLIC OLEFINS, OR ARENES ON A DIRHODIUM CENTRE**

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

The complex $\text{Cp}_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ ¹ readily adds a variety of organic substrates including alkynes,² carbenes³ and nitrenes.⁴ In these reactions, initial coordinative addition of the substrate is followed by intramolecular reactions in which new C-C and/or C-N bonds are formed. The corresponding reactions with olefins proceed in a different manner. There is initial C-H bond cleavage to give a Rh_2 - μ -alkylidene system, and the released H migrates to the $\text{CF}_3\text{C}_2\text{CF}_3$ ligand to generate a second Rh_2 - μ -alkylidene system:



The reaction occurs rapidly (10-30 min.) when solutions of $\text{Cp}_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ and acyclic olefins (e.g. $\text{H}_2\text{C}=\text{CH}_2$, $\text{H}_2\text{C}=\text{CHMe}$, *cis*- $\text{MeCH}=\text{CHMe}$), conjugated dienes (e.g. $\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$, $\text{H}_2\text{C}=\text{C}=\text{CMe}_2$) or cyclic olefins (e.g. cyclooctene, norbornadiene) are exposed to sunlight. With arenes (e.g. C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$), the simultaneous activation of two C-H bonds is observed and products such as $[\text{Cp}_2\text{Rh}_2\{\mu\text{-C}(\text{CF}_3):\text{CH}(\text{CF}_3)\}_2(\mu, \mu'\text{-C}_6\text{H}_4)]$ are formed. In the reaction with acrylonitrile, an intermediate of formula $\text{Cp}_2\text{Rh}_2(\text{CO})(\text{H}_2\text{C}=\text{CHCN})(\text{CF}_3\text{C}_2\text{CF}_3)$ can be isolated and subsequently converted to $\text{Cp}_2\text{Rh}_2(\mu\text{-CH}=\text{CHCN})\{\mu\text{-C}(\text{CF}_3)=\text{CH}(\text{CF}_3)\}$. The crystal structure of the latter complex has been determined. The reactions with fluoroolefins occur in a different manner. For example, $\text{F}_2\text{C}=\text{CF}_2$ gives two binuclear metallocyclic products $[\text{CpRh}]_2\{\mu\text{-CF}=\text{CFCOC}(\text{CF}_3)=\text{C}(\text{CF}_3)\}$ and $[\text{CpRh}]_2(\mu\text{-CO})\{\mu\text{-CF}_2\text{CF}_2\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\}$.

1. R.S. Dickson, A.P. Oppenheim and G.N. Pain, *J. Organomet. Chem.*, **224**, 377 (1982).
2. P.A. Corrigan, R.S. Dickson, S.H. Johnson, G.N. Pain and M. Yeoh, *Aust. J. Chem.*, **35**, 2203 (1982).
3. R.S. Dickson, G.D. Fallon, R.J. Nesbit and G.N. Pain, *Organometallics*, **4**, 355 (1985).
4. R.S. Dickson, R.J. Nesbit, H. Pateras, J.M. Patrick and A.H. White, *J. Organomet. Chem.*, **265**, C25 (1984).

SOLID AND SOLUTION STUDIES OF A NEW AND UNUSUAL MIXED VALENT
TE(VI)-TE(IV) COMPLEX.

D. Dakternieks, R. Di Giacomo, R.W. Gable and B.F. Hoskins;
Department of Inorganic Chemistry, University of Melbourne, Parkville.

The new compound hexakis[{2-(diethoxythiophosphorylthio)-1,3-dihydro-2 λ^4 -benzotellurole-2-yl}oxy]tellurium(VI), $\text{Te}\{\text{O}(\text{C}_6\text{H}_8)\text{Te}[\text{S}_2\text{P}(\text{OEt})_2]\}_6$, has been synthesized under extremely mild conditions. This appears to be the first organotellurium compound containing both tellurium(VI) and tellurium(IV). The crystal structure shows a central tellurium(VI) atom in an octahedral environment of oxygens. The oxygens bridge to six organotellurium(IV) centres, each of which is effectively seven coordinate in a geometry best described as bicapped trigonal-bipyramidal. The seventh coordination position is occupied by a stereochemically active lone pair. There is extensive secondary bonding from sulphur atoms to adjacent tellurium atoms. These secondary bonds appear to persist in solution over a wide temperature range, where two tellurium-125 signals of equal intensity are observed for the tellurium(IV) centres.

The parent compound $\underline{\text{S}}, \underline{\text{S}}'-(1,3\text{-dihydro-}2\lambda^4\text{-benzotellurole-}2,2\text{-diyl})\underline{\text{O}}, \underline{\text{O}}, \underline{\text{O}}', \underline{\text{O}}'$ tetraethylbis(dithiophosphate), $\text{C}_8\text{H}_8\text{Te}[\text{S}_2\text{P}(\text{OEt})_2]_2$, which also displays secondary bonding in the solid state, is effectively eight coordinate with the geometry about tellurium a distorted dodecahedron. A stereochemically active lone pair occupies the eighth position. The secondary bonds in this case do not persist in solution, with the geometry apparently reducing to trigonal-bipyramidal.

SOLID AND SOLUTION STUDIES OF A NEW AND UNUSUAL MIXED VALENT
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The new compound hexakis[$\{2-(\text{diethoxythiophosphorylthio})-1,3\text{-dihydro-}2\lambda^4\text{-benzotellurole-2-yl}\}\text{oxy}\}\text{tellurium(VI)}$], $\text{Te}\{\text{O}(\text{C}_8\text{H}_8)\text{Te}[\text{S}_2\text{P}(\text{OEt})_2]\}_6$, has been synthesized under extremely mild conditions. This appears to be the first organotellurium compound containing both tellurium(VI) and tellurium(IV). The crystal structure shows a central tellurium(VI) atom in an octahedral environment of oxygens. The oxygens bridge to six organotellurium(IV) centres, each of which is effectively seven coordinate in a geometry best described as bicapped trigonal-bipyramidal. The seventh coordination position is occupied by a stereochemically active lone pair. There is extensive secondary bonding from sulphur atoms to adjacent tellurium atoms. These secondary bonds appear to persist in solution over a wide temperature range, where two tellurium-125 signals of equal intensity are observed for the tellurium(IV) centres.

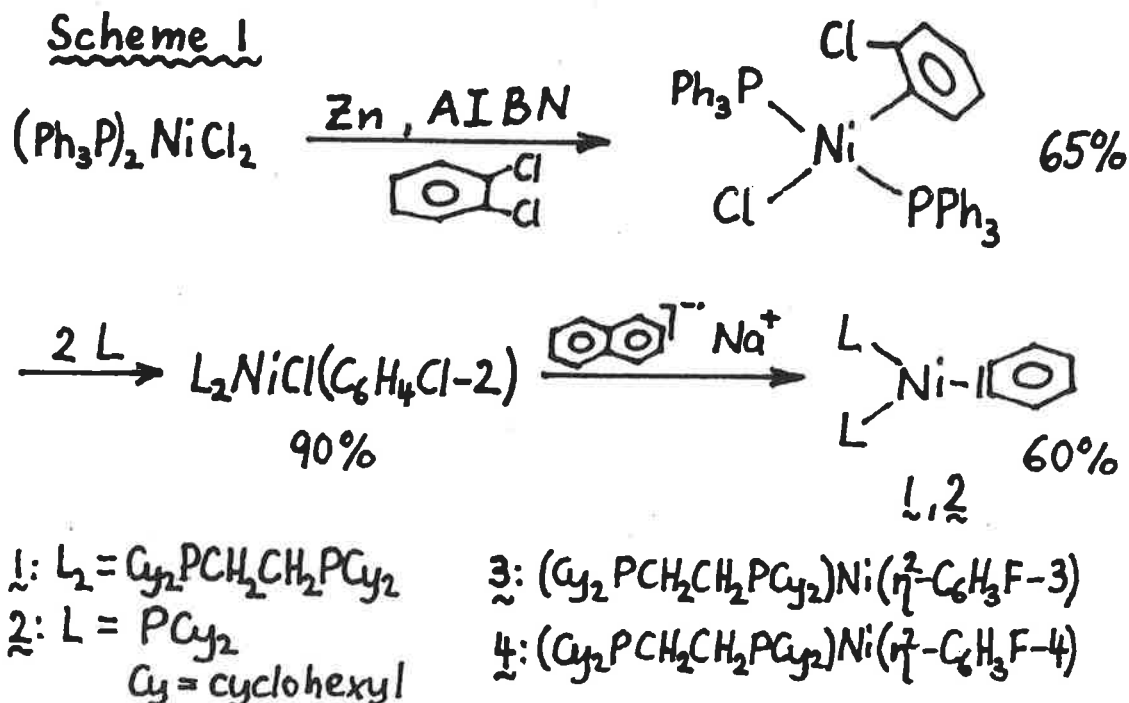
The parent compound $\underline{\text{S}}, \underline{\text{S}}'-(1,3\text{-dihydro-}2\lambda^4\text{-benzotellurole-2,2-diyl})\underline{\text{O}}, \underline{\text{O}}, \underline{\text{O}}', \underline{\text{O}}'$ tetraethylbis(dithiophosphate), $\text{C}_8\text{H}_8\text{Te}[\text{S}_2\text{P}(\text{OEt})_2]_2$, which also displays secondary bonding in the solid state, is effectively eight coordinate with the geometry about tellurium a distorted dodecahedron. A stereochemically active lone pair occupies the eighth position. The secondary bonds in this case do not persist in solution, with the geometry apparently reducing to trigonal-bipyramidal.

NICKEL-BENZYNE AND -BENZDIYNE COMPLEXES

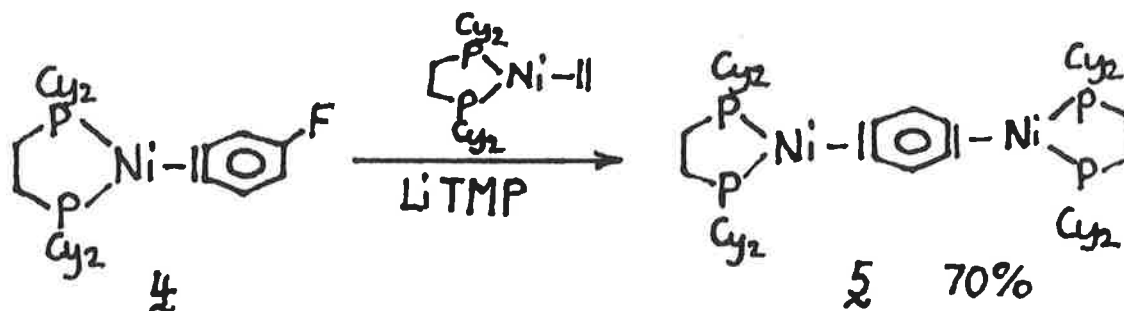
M.A. Bennett, N.K. Roberts, J.S. Drage, and H.P. Schwemlein

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Canberra, Australia

Benzyne (1,2-dehydrobenzene, C_6H_4) is a highly reactive species, observable only under low temperature matrix conditions. Surprisingly, there are very few cases wherein the C_6H_4 fragment is stabilized as a ligand in a mononuclear metal complex. In Scheme I we present a general synthetic approach to bis(tertiary phosphine) nickel n^2 -benzyne compounds **1** and **2** and the fluoro-benzyne derivatives **3** and **4**.



Complex **1** was prepared more directly by treating $(Cy_2PCH_2CH_2PCy_2)NiCl_2$ with magnesium and bromochloro benzene. Halide salts of magnesium, lithium and mercury (II) reacted with **1** to give stable adducts which are currently being characterized. Remarkably, fluoro-benzyne complex **4** reacted with excess lithium tetramethylpiperide (LiTMP) and $(Cy_2PCH_2CH_2PCy_2)Ni(n^2-C_2H_4)$ to give a 70% yield of 1,4-benzdiyne complex **5**, which was characterized by X-ray diffraction. This species



is the first complex of the hitherto unobserved C_6H_2 fragment. Work is underway toward preparing the 1,3-benzdiyne isomer.

" The Electronic Spectrum of $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ "

Lucjan Dubicki, Elmars Krausz^a and Robert Stranger.^b

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The crystal structure of $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ indicates significant Mo-Mo ($t_2^3-t_2^3$) bonding¹ which consists of a moderately strong σ bond and two very weak δ bonds.² The electronic spectrum in the near IR region resembles superficially the spectrum of $[\text{MoCl}_6]^{3-}$. A single crystal spectroscopic study shows that the highly structured absorption at $1400-12650\text{ cm}^{-1}$ has no MCD and therefore consists of spin singlet and orbitally nondegenerate states. Furthermore, new absorption lines are found near 11600 cm^{-1} and 7800 cm^{-1} , both having MCD and the latter having well resolved Zeeman splittings.

Many of the features of the electronic spectrum can be qualitatively explained on the basis of the generalized exchange Hamiltonian.^{3,4} The strong $t_{20}-t_{20}$ interaction stabilizes those pair states which correlate with the states of the $t_{2\pm}-t_{2\pm}$ configuration. However the t_{20} electrons are not "perfectly paired off". In particular the ground multiplet is described by $J_{ab} \underline{S}_a \underline{S}_b$ (d^2-d^2), but J_{ab} is dominated by $t_{20}-t_{20}$ kinetic exchange.

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3. K.W.H. Stevens, Phys.Rept.24C,1(1976).
4. N.Fuchikami and Y.Tanabe, J.Phys.Soc.Japan.47,505(1979).

THE STRUCTURAL NATURE OF BIS(O-BENZYLXANTHATO)NICKEL(II)
AND THE BENZENE CLATHRATE OF ITS 1,10-PHENANTHROLINE ADDUCT

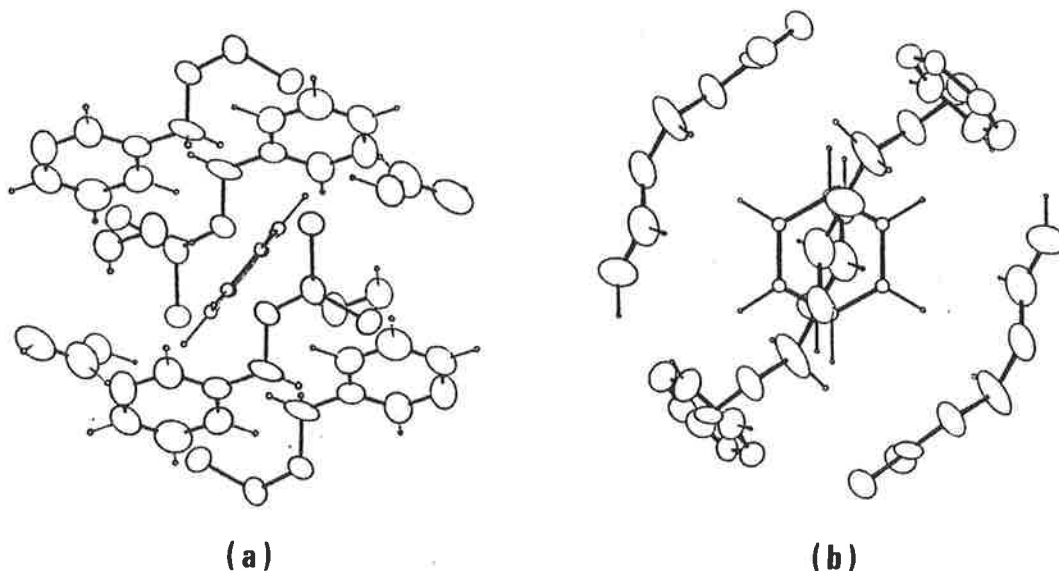
Alison Edwards, George Winter and Bernard Hoskins.

Department of Inorganic Chemistry, University of Melbourne.

The structures of the title compounds have been determined using single crystal, X-ray diffraction methods.

In crystals of nickel benzylxanthate, the nickel-sulphur bonds are asymmetric, which is atypical of transition metal xanthates. It is proposed that a weak but significant interaction between one sulphur of each xanthate ligand with the nickel atom of the adjacent molecule is the cause of this asymmetry.

Crystals of the adduct were grown from a benzene solution and formed as the benzene clathrate. The cavity in which the benzene ring is enclosed is approximately $5 \times 7 \times 11$ Å, views of the cavity (a) parallel and (b) perpendicular to the benzene ring are shown below. On formation of the adduct the dihedral angle between the NiS_2C and C_6H_5 moieties of the xanthate ligand is reduced by 28.7° .



**THE SYNTHESIS OF HETEROBINUCLEAR μ -OXO BRIDGED COMPOUNDS
OF Cr^{III} with Fe^{III} , Mn^{III} and Mo^{V}**

Robyn L. Elliott, Peter J. Nichols and Bruce O. West

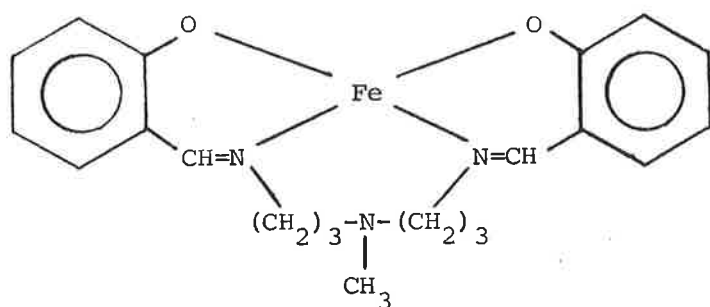
Department of Chemistry, Monash University, Clayton, Victoria 3168.

The synthesis of heterobinuclear oxo bridged complexes containing Cr^{III} and Fe^{III} with porphyrin ligands attached, $[(\text{P})\text{CrOFe}(\text{P})]$ has been achieved by reaction between $(\text{P})\text{Cr}^{\text{IV}}\text{O}$ and $\text{Fe}^{\text{II}}(\text{P})$ derivatives.¹

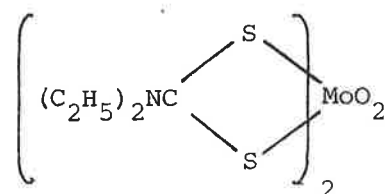
Similar reactions have now been found to occur between $\text{Cr}^{\text{IV}}\text{O}(\text{TPP})$ (TPP = dianion of 5,10,15,20-tetraphenylporphyrin) and Fe^{II} , Mn^{II} and Mo^{IV} complexes containing O_2N_3 , O_2N_2 , S_2N_2 and S_2 donor ligands such as salicylideneimines, thiosalicylideneimines and dithiocarbamates. The Cr-O-Fe and Cr-O-Mo complexes show antiferromagnetic coupling between the metal, e.g. μ_{eff} per molecule for $(\text{TPP})\text{Cr}^{\text{III}}\text{OFe}^{\text{III}}(\text{salmah})$ (i) is 3.2 B.M.; for $(\text{TPP})\text{Cr}^{\text{III}}\text{OMo}^{\text{V}}(\text{O})(\text{Et}_2\text{dtc})_2$ (ii) 3.6 B.M. The Cr-O-Mn complexes also display evidence for magnetic coupling although to a reduced degree, thus $(\text{TPP})\text{Cr}^{\text{III}}\text{OMn}^{\text{III}}(\text{salmah})$ has $\mu_{\text{eff}} = 5.3$ B.M. while the spin only value for an uncoupled d^3 - d^4 system is 6.24 B.M. The Mössbauer spectrum of $(\text{TPP})\text{CrOFe}(\text{salmah})$ indicates that the Fe^{III} species has $S = 5/2$ indicating a similar antiferromagnetic coupling mechanism to that described for the Cr-O-Fe porphyrin derivatives.¹

The complexes have been isolated in most instances as monohydrates and other Lewis bases readily coordinate to the complexes, presumably to Cr. The attachment of pyridine to $(\text{TPP})\text{CrOFe}(\text{salmah})$ has $\log K = 1.4$.

The heterobinuclear oxo complexes are stable in solution under nitrogen for substantial periods of time but on exposure to moist air, decomposition occurs, e.g. $(\text{TPP})\text{CrOFe}(\text{salen})$ decomposes to yield the sparingly soluble $[\text{Fe}(\text{salen})]_2\text{O}$ and $\text{CrO}(\text{TPP})$.



(i) $\text{Fe}(\text{salmah})$

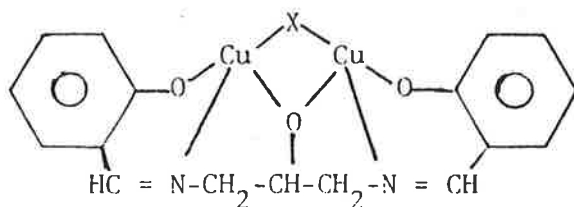


(ii) $\text{MoO}_2(\text{Et}_2\text{dtc})_2$

1. Liston, D.J., Kennedy, B.J., Murray, K.S. and West, B.O., *Inorg. Chem.*, **24**, 1561 (1985).

BINUCLEAR COPPER (II) COMPLEXES OF SOME SCHIFF BASE LIGANDS

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Department of Chemistry, University of Wollongong
and Ekk Sinn
Department of Chemistry, University of Virginia



Binuclear Copper (II) complexes of the type Cu_2LX have been synthesised where:

X = Alkanoates, Benzoates, Pyrazolate

The structure and properties of these complexes are affected by the nature of the bridging ligand "X" and by the presence of a solvent molecule bonded to one copper atom. The angle between the principal copper planes varies between 8° and 61° and the Cu-Cu separation varies from 3.53\AA to 3.14\AA .

Lewis acidity of bis(ethane-1,2-dithiolato)tin(IV) in benzene solution

Y. Farhangi

Department of Chemistry ,University of Alzahra,Tehran,IRAN.

The technique of calorimetric titration has been used to obtain thermodynamic data for the formation of 1:1 and 1:2 adducts of SnS_4 with different bidentate and unidentate Lewis bases in benzene solution at 30°C . The tin atom is six-coordinate in both 1:1 and 1:2 adducts, the following data have been obtained for 1:1 adducts :

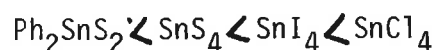
Lewis bases	K	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$
1,10-Phen	$> 10^4$	77.63	> 23.2	< 180
2,2'-Bipy	1.19×10^3	64.4	17.8	170
Tmen	6.90×10^3	80.10	22.27	189

(K in l.mol^{-1} , $\Delta H^\circ, \Delta G^\circ$ in kJ.mol^{-1} , ΔS° in $\text{J.K}^{-1}.\text{mol}^{-1}$)

The data for 1:2 adducts are :

Lewis bases	K_{12}	$-\Delta H_{12}^\circ$
BuNH_2	1.60×10^4	93.25
Py-NO	1.46×10^3	57
Pip	7000	73
4-Mepy	700	84
Py	160	82

The resolved $K_1, K_2, \Delta H_1^\circ$ and ΔH_2° would be presented. This work shows that the following order of Lewis acidity may be drawn for the tin(IV):



2-Mepy, DMSO, NBu_3 , NMe_3 , and Bu_2NH do not react with the titled compound in benzene solution ,while 1:2 adducts of these bases are isolated in the solid state.

Investigations of the Stereochemistry of Hypervalent
Tellurium Compounds: Crystal Structures of some
Organotellurium(IV) 1,1-Dithiolates

Dainis Dakternieks, Robert Di Giacomo,
Robert W. Gable and B. F. Hoskins.

Department of Inorganic Chemistry,
University of Melbourne,
Parkville, Australia, 3052.

The crystal structures of a series of organotellurium(IV) complexes, $\text{C}_8\text{H}_8\text{Te}[\text{S}_2\text{CNet}_2]_2$, $\text{C}_8\text{H}_8\text{Te}[\text{S}_2\text{COEt}]_2$, $\text{MeTe}[\text{S}_2\text{CNet}_2]_2\text{I}$ and $\text{PhTe}[\text{S}_2\text{CNet}_2]_2[\text{S}_2\text{P}(\text{OEt})_2]$ have been determined by single-crystal, X-ray diffraction methods. In all these complexes the lone pair at the tellurium(IV) is stereochemically active, occupying a position in the primary coordination sphere of the tellurium atom. The degree of secondary bonding varies with the nature of the organo- groups and the 1,1-dithiolate ligands, and gives rise to a variety of structures ranging from a pentagonal bipyramid for $\text{MeTe}[\text{S}_2\text{CNet}_2]_2\text{I}$, to a bicapped trigonal bipyramid for $\text{C}_8\text{H}_8\text{Te}[\text{S}_2\text{CNet}_2]_2$. The structures of $\text{C}_8\text{H}_8\text{Te}[\text{S}_2\text{COEt}]_2$ and $\text{PhTe}[\text{S}_2\text{CNet}_2]_2[\text{S}_2\text{P}(\text{OEt})_2]$ are best described as dodecahedral.

SQUARE PLANAR AND OCTAHEDRAL COMPLEXES OF A LINEAR OCTAAZA LIGAND

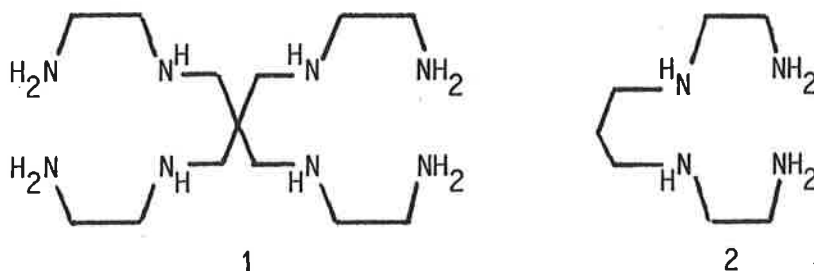
Lawrence R. Gahan, Mark A. Kingston and Kon A. Nicolaidis

Department of Chemistry, University of Queensland, St Lucia 4067

The ligand 5,5-bis(4-amino-2-azabutyl)-3,7-diaza-1,9-diaminononane (tabm) (1) has been prepared from reaction between benzenesulfonated pentaerythritol and ethane-1,2-diamine.

The ligand may be considered either as -

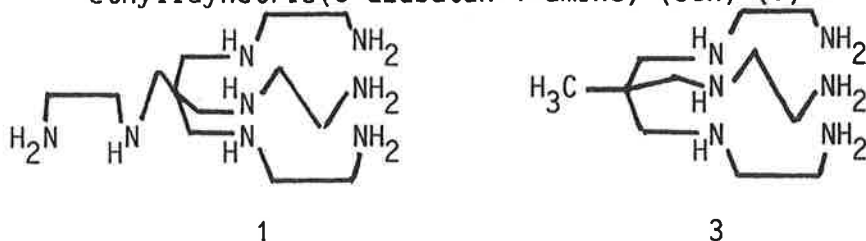
- (a) a dimeric analogue of the linear tetraamine 3,7-diaza-1,9-diaminononane (2,3,2-tet) (2) -



In this configuration bis-copper(II) and bis-cobalt(III) complexes have been prepared.

or

- (b) as an analogue of the hexamine ligand 4,4',4''-ethylidynetris(3-azabutan-1-amine) (sen) (3) -



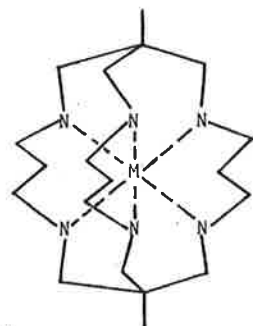
In this configuration the cobalt(III) complex has been prepared. Attempts have been made to encapsulate the metal ion to produce a cage complex bearing a pendant arm suitable for further synthetic elaboration.

SYNTHESIS OF D_3 SYMMETRIC LARGE CAVITY RHODIUM CAGE SYSTEMS

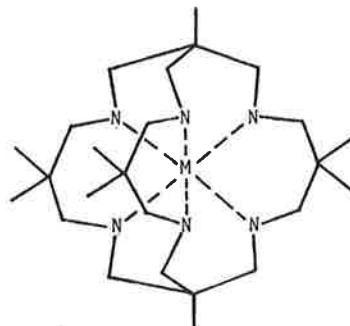
R.J. Geue, M.B. McDonnell and A.M. Sargeson

Research School of Chemistry, The Australian National University, Canberra, A.C.T. 2601

We have recently been exploring several approaches to the development of a suitable template synthesis for D_3 symmetric large cavity mononuclear cage systems of the types 1 and 2. Although the low spin cobalt(III) N_6 chromophore has often been used as a template



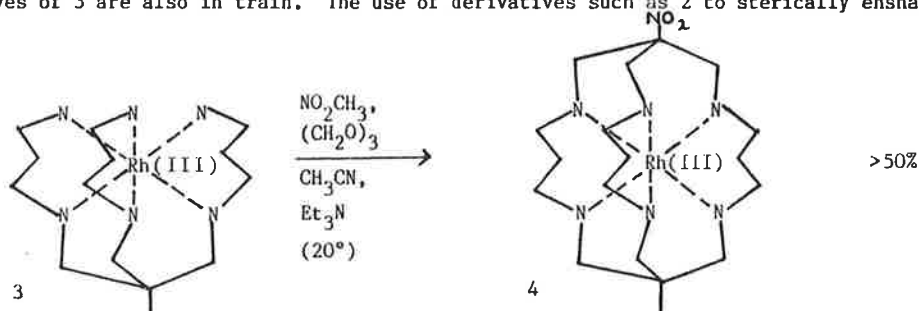
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2

for generating smaller macrobicyclic ligands,¹ the larger cavities of 1 and 2 would appear from molecular and force field models to require M-N distances of over 2.05 Å, a little too long for inert Co(III)-N bonds. This is largely necessary to accommodate steric interactions between the methylene groups of the ligands, and our attention has now turned toward larger metal-nitrogen templates, and non-aqueous media to inhibit the hydrolysis of active intermediates.

A refined method for encapsulation in non-aqueous CH_3CN using $(CH_2O)_3$ polymer, NO_2CH_3 and Et_3N as organic reagents, has proved particularly attractive because only small excesses of reagents are required, and intermediates (Co-N=CH₂ imines) appear to be longer lived and more stable than in aqueous media. This procedure was applied to the Rh(stn) substrate 3 (as Rh-N distances are ≥ 2.05 Å²) and has yielded the first hexaazatricosane cage system 4, with a cavity size capable of encapsulating the larger transition metal ions in their normal oxidation states. The experiment is an astonishingly facile example of Rhodium-coordinated amine reactivity, requiring only ~30 minutes at room temperature under our conditions. Similar experiments with more labile M(III) metals and using the methylated derivatives of 3 are also in train. The use of derivatives such as 2 to sterically ensnare



smaller metals (or high oxidation states), and generate powerful, stable oxidising agents is an intriguing prospect.

A discussion of the method, and spectral and NMR (¹H and ¹³C) evidence for the new cage system will be presented.

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2. M.F. Gargallo, R.E. Tapscott and E.N. Duesler, Inorg. Chem., 1984, 23, 918.

THE SYNTHESIS OF $\text{OsCl}_2(\text{CO})_2(\eta^1\text{-dppm})_2$ AND ITS
USE AS A SYNTHETIC PRECURSOR TO HETEROBINUCLEAR
COMPLEXES.

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Jenkins. Department of Chemistry, Dalhousie University,
Halifax, N.S., Canada.

$\text{OsCl}_2(\text{CO})_2(\eta^1\text{-dppm})_2$ can best be prepared by reacting $\text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2$ with excess dppm under CO pressure (60 psi @ 150°C, to inhibit chelation) in xylene. Reacting $\text{OsCl}_2(\text{CO})_2(\eta^1\text{-dppm})_2$ with substrates such as $[\text{RhCl}(\text{COD})]_2/\text{CO}$, $\text{IrCl}(\text{CO})_2(\text{p-toluidine})$ or $\text{PtCl}_2(\text{PhCN})_2$ results in dichloromethane insoluble, polymeric derivatives. Binuclear complexes can be derived at, however, via a transmetallation technique or by employing substrates capable of forming a metal-metal bond through oxidative addition across an Os-Cl bond.

Reacting a solution of $\text{OsCl}_2(\text{CO})_2(\eta^1\text{-dppm})_2$ with solid $\text{Ag}(\text{NO}_3)$ or $\text{Ag}(\text{ClO}_4)$ results in the formation of $[\text{OsCl}_2(\text{CO})_2(\text{dppm})_2.\text{Ag}]\text{Y}$ ($\text{Y} = \text{NO}_3$, ClO_4). Treatment of either of these compounds with LiCl gives $\text{OsCl}_2(\text{CO})_2(\text{dppm})_2.\text{AgCl}$. With the Rh, Ir and Pt substrates above, $[\text{OsCl}_2(\text{CO})_2(\text{dppm})_2.\text{Ag}]\text{ClO}_4$ reacts to give the binuclear complexes $[\text{OsCl}_2(\text{CO})_2(\text{dppm})_2.\text{ML}]\text{ClO}_4$ ($\text{M} = \text{Rh}, \text{Ir}, \text{L} = \text{CO}$; $\text{M} = \text{Pt}, \text{L} = \text{Cl}$) and AgCl . Also, $\text{Fe}_2(\text{CO})_9$ reacts with $\text{OsCl}_2(\text{CO})_2(\eta^1\text{-dppm})_2$ to give $[\text{OsFeCl}_2(\text{CO})_5(\mu\text{-dppm})_2]\text{Cl}$ but fails to react with $(\text{PPN})\text{FeH}(\text{CO})_4$.

SYNTHESIS AND ELECTROCHEMICAL STUDIES ON BINUCLEAR RUTHENIUM AND OSMIUM COMPLEXES BRIDGED BY 2,2'-BIBENZIMIDAZOLATE ANION

Masa-aki Haga* and Takeko Matsumura-Inoue**

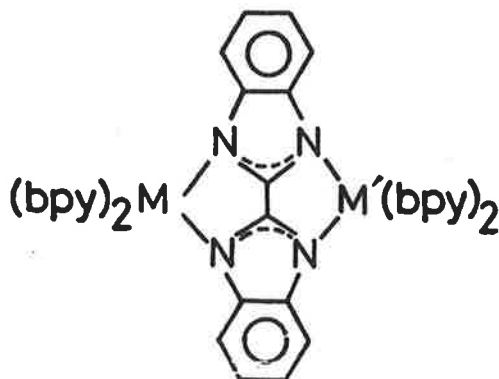
*Department of Chemistry, Faculty of Education, Mie University, 1515 Kamihama, Tsu, Mie 514, Japan.

** Department of Chemistry, Nara University of Education, Takahata, Nara, Japan.

The nature of metal-metal interaction in the binuclear complexes can be systematically changed by the selection of bridging ligand. Herein anionic 2,2'-bibenzimidazolate (BiBzIm) is used as two symmetrical bidentate bridging ligand.

New homo- and heterobinuclear Ru and Os binuclear complexes, $[(bpy)_2M(BiBzIm)M'(bpy)_2](ClO_4)_2$ ($M = Ru$ and Os ; $M' = Ru, Os, Co$, and Ni), have been synthesized. The binuclear Ru-Ru, Os-Os, Ru-Os, and Ru-Co complexes undergo two successive one-electron oxidation processes, while the Ru-Ni complex exhibits only one reversible Ru(II/III) oxidation process. The Ru(II/III) and Os(II/III) oxidation potentials for the binuclear complexes are dependent on the ionic charge of metal ions in the second site. The observed Ru(II/III) oxidation potentials are $\sim +0.78$ V and $\sim +1.0$ V vs SCE for +2 and +3 charged second metal ions, respectively. This result suggests that the electrostatic interaction contributes to a major factor to determine the potentials in this system.

The mixed-valence Os(II) - Os(III) and Ru(II) - Os(III) complexes show the rich near-infrared spectra. The assignment of these near-infrared bands will be also discussed in terms of the orbital splitting by the spin-orbit coupling.



**LIGAND OXIDATION AND PROTON EXCHANGE IN Fe HEXAAMINE CAGE COMPLEXES:
STRUCTURE OF A DIIMINE OXIDATION PRODUCT.**

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The isotropic shifts of the ^1H NMR resonances of Fe(II) cages (1) in basic aqueous solution exhibit a marked isotope effect upon H/D exchange. This is due to a shift in the spin equilibrium between high and low-spin Fe(II)¹ and resonances of all seven isotopomers are resolved (Figure 1).

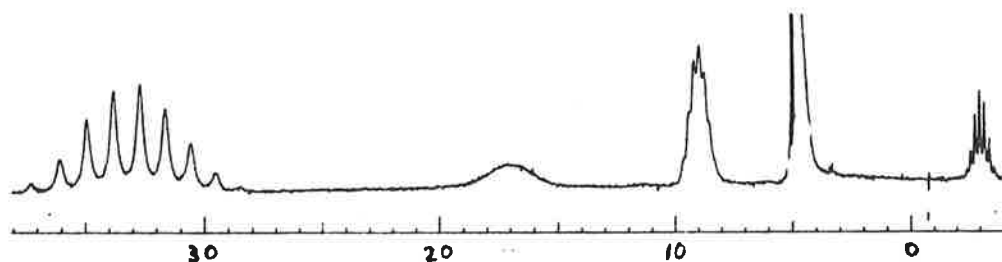
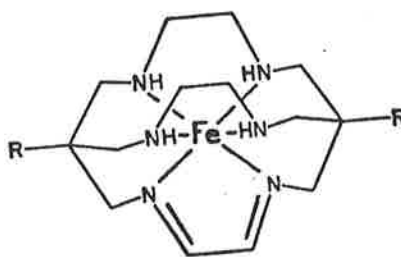


Figure 1. ^1H NMR (200 MHz) of $[\text{Fe sar}]^{2+}$ in $1\text{M OD}^-/\text{D}_2\text{O}$.

The Fe(III) cage complex disproportionates in base to give Fe(II)hexaamine (1) and Fe(II)diimine (2) cage complexes. Mechanistic details of formation of 2 and the crystal structure of one such complex will be presented.



1



2

R = H, NH_2 or NH_3

1. See L.L. Martin, et al's poster at this conference.

Molecular Mechanics Modelling of the Interaction of
Cis-diamineplatinum(II) complexes with DNA fragments

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Department of Inorganic Chemistry, University of Sydney,
Sydney 2006, Australia

A number of cis-diaminedichloroplatinum(II) complexes are potent anti-cancer agents. There is considerable evidence¹ that the mechanism of action of these drugs involves the formation of an intra-strand crosslink between adjacent guanosine nucleotides of DNA by coordination of platinum to the nucleophilic N(7) atom of each guanosine.

We have developed a force field for molecular mechanics analysis of the interaction of platinum with guanosine nucleotides by modelling $[\text{Pt}(\text{NH})_2(9\text{-ethylguanine})_2]^{2+}$, $[\text{Pt}(\text{NH}_3)_2(\text{guanosine})_2]^{2+}$, and $[\text{Pt}(\text{NH}_3)_2(\text{inosine } 5'\text{-monophosphate})]^{2+}$. Using this force field the complexes between the nucleotide fragment deoxycytidyl-(3',5')-deoxycytidine:deoxyguanyl-(3',5')-deoxyguanosine (CpC:GpG) and various diamineplatinum(II) moieties are being studied. The influence of the specific diamine ligand(s) employed, and of the role of hydrogen bonding, on the ability of platinum to bond to DNA is being analyzed.

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* ADSORPTION OF DYES BY ZSM-5 ZEOLITES

G.P. Handreck

Department of Chemistry

Monash University

1985

The aluminium III, gallium III, iron III and scandium III forms of the high silica zeolite ZSM-5 adsorb the cationic dyes methylene blue and crystal violet to varying degrees over the full range of the M_2O_3/SiO_2 ratios possible for the ZSM-5 zeolite.

The Al-ZSM-5 zeolite dye adsorption rises to a plateau. After a steady rise, dye adsorption for Ga-ZSM-5 zeolites declines due to a reversion to silicalite, as shown by x-ray diffraction measurements. Fe-ZSM-5 and Sc-ZSM-5 zeolites show a similar decline, but at lower ratios.

Polarity of the external surface of the Fe-ZSM-5 zeolites, as measured by 4-nitroanisole adsorption and detected by reflectance spectroscopy, increases markedly at a Fe_2O_3/SiO_2 ratio at which cationic dye adsorption declines.

Spectroscopic Examination of Inhibitor and Peptide Intermediate
Complexes of Carboxypeptidase A α .

Graeme R. Hanson, Richard Martinelli, Barton Holmquist and Bert L. Vallee

Center for Biochemical and Biophysical Sciences and Medicine,
Harvard Medical School, Boston 02115 USA.

Equilibrium trapping of the peptide intermediates from cobalt carboxypeptidase A α (CoCPA) has enabled Electron Paramagnetic Resonance (EPR) and Electronic Absorption Spectroscopy to be used in their characterization. A number of singly and multiply bound inhibitor complexes of CoCPA have also been examined with EPR and electronic absorption spectroscopy. The second binding mode of the multiple binding inhibitors exhibits similar spectral properties to those of the peptide intermediates suggesting a similar metal coordination sphere for the cobalt ion in the peptide intermediates of CoCPA.

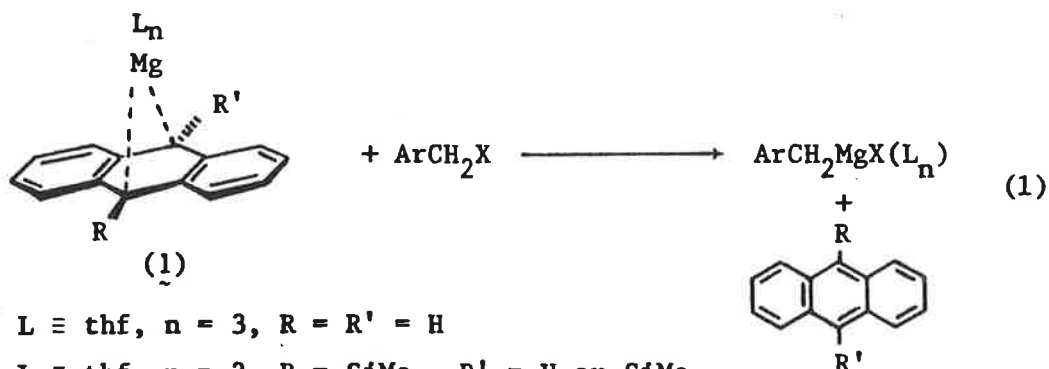
Magnesium(Anthracene) Complexes: Their Utility in the
Synthesis of Grignard Reagents

Stephen Harvey, Peter C. Junk, Colin L. Raston and Geoffrey Salem.

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A., 6009.

Grignard reagents feature extensively as carbanion transfer reagents in alkyl-metal chemistry and in organic synthesis. We have developed a new method of preparing Grignard reagents in almost quantitative yield from benzylic halides where established methods of Grignard formation, including the use of finely divided metal (Rieke's magnesium) fail or are unreliable. It is the reaction of a magnesium anthracene complex, (1), with a benzylic halide, usually a chloride (equation 1). Some novel Grignard reagents prepared include (2) - (4).¹

Compound (1), $L = \text{thf}$, $R = R' = \text{H}$ formed on treating magnesium with anthracene in thf has been described by several research groups.² Other compounds of (1) are new and their syntheses, in some cases by more than one route, will be described. In contrast to (1), $L = \text{thf}$, $R = R' = \text{H}$ the tmedc complex is stable in OEt_2 and toluene in which Grignard reagents can be prepared.



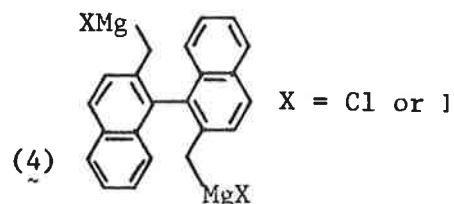
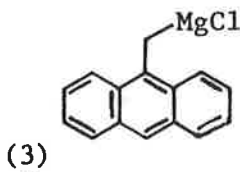
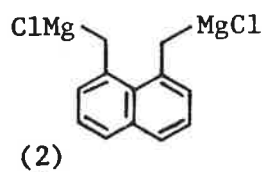
$L \equiv \text{thf}$, $n = 3$, $R = R' = \text{H}$

$L \equiv \text{thf}$, $n = 2$, $R = \text{SiMe}_3$, $R' = \text{H}$ or SiMe_3

$L_n = (\text{thf})(\text{tmeda})$, $R = R' = \text{H}$

[thf \equiv tetrahydrofuran

tmeda \equiv N,N,N',N'-tetramethylethylenediamine]



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2. H.E. Ramsden, US Pat. 3354190, 1965; Chem. Abstr., 1968, 68, 114744e;
P.K. Freeman and L.L. Hutchinson, J. Org. Chem., 1983, 48, 859;
B. Bogdanović, S. Liao, R. Mynott, K. Schlichte, and U. Westeppe, Chem. Ber., 1984, 117, 1378.

Light Induced Excited Spin State Trapping in $\text{Fe}(\text{ptz})_6(\text{BF}_4)_2$ and $\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6(\text{BF}_4)_2$ (ptz = 1-propyltetrazole)

A. Hauser, Research School of Chemistry, A.N.U., Canberra ACT 2601

$\text{Fe}(\text{ptz})_6(\text{BF}_4)_2$ is an iron(II) spin crossover system which shows light induced excited spin state trapping (LIESST), i.e. by irradiating into the $^1A_1 \rightarrow ^1T_1$ absorption band at temperatures below 50 K, where it is in the low spin state, the system can be trapped in the high spin state [1]. Above 50 K relaxation back to the 1A_1 state, with a marked deviation from first order kinetics, as a result of strong cooperative lattice effects, takes place [1].

In $\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6(\text{BF}_4)_2$ ($x \approx 0.1$) LIESST is also observed, but in this case the relaxation follows first order kinetics with a frequency factor $k_0 \sim 10^5/\text{sec}$ and an activation energy $\Delta E \approx 800 \text{ cm}^{-1}$. This shows that LIESST is basically a single ion phenomenon.

In Fig. 1 a possible mechanism for LIESST is indicated, involving intersystem crossing to a low lying 3T_1 state and from there to the 5T_2 state, where at sufficiently low temperatures the system remains trapped. This mechanism predicts that the effect should be reversible, and this is indeed found to be the case.

A quantitative kinetics study both in the forward and reverse direction of LIESST showed its efficiency to be $\sim 0.5\%$ for the former and $\sim 0.1\%$ for the latter. In contrast to the thermal $^5T_2 \rightarrow ^1A_1$ relaxation cooperative lattice effects in LIESST itself are of little importance.

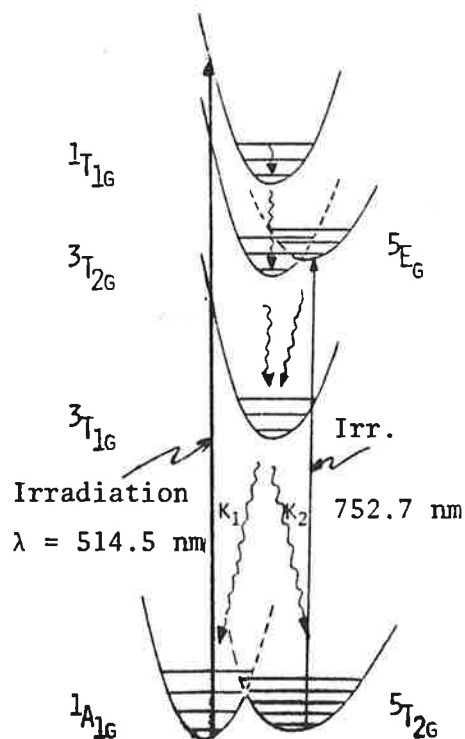


Fig. 1

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VANADIUM CHEMISTRY RELEVANT TO ASCIDIANS

S.G. Brand, C.J. Hawkins, and T. Kabanos

Department of Chemistry
University of Queensland
ST LUCIA Q 4067

High concentrations of vanadium have been known to exist in the blood cells of certain species of ascidian for the past 75 years. Recently the occurrence, concentration, and oxidation state of vanadium have been related to the phylogeny of the Ascidiacea. This paper reports further studies on the oxidation state and location of vanadium within the blood cells and on the intracellular reactions of exogenous ligands such as 2,2'-bipyridine with the vanadium.

The ESR spectra of "whole animals" under anaerobic conditions show strong vanadium(IV) spectra for a range of aplousobranchs, and barely detectable vanadium(IV) spectra for phlebobranchs. However, when sliced animals are exposed to air, the signals for both sub-orders increase markedly. The spectra at 77K have been analysed for the A and g parameters and these have been related to the phylogeny and to the mode of coordination. The fact that the spectra increase in size on oxidation indicates vanadium(III) is present in both sub-orders. This has been confirmed by reacting 2,2'-bipyridine intracellularly with the vanadium. The purple compound formed can be synthesised only from vanadium(III). It is an oxo bridged binuclear complex with the two vanadiums formally in oxidation state III. The structure, properties and reactions of this compound will be described.

1. C.J. Hawkins, P. Kott, D.L. Parry and J.H. Swinehart,
Comp.Biochem.Physiol. 76B, 555 (1983).

HIGH RESOLUTION SOLID STATE ^{31}P NMR SPECTROSCOPY OF COINAGE
METAL-TRIPHENYLPHOSPHINE COMPLEXES.

Peter C. Healy, Jeffrey C. Dyason, Peter F. Barron and
Allan H. White.

High-resolution CPMAS Solid State ^{31}P NMR Spectra of the adducts of copper(I) halides with triphenylphosphine give well resolved quartets in which the splitting parameters are a function of the stereochemical environment of the 'spectroscopically invisible' copper(I) atom.

The magnitude of the splitting, $\Delta\nu_i$, is a function of both Cu-P scalar coupling and Cu-P dipolar and J tensor interactions which are not averaged out by the magic angle spinning techniques. This latter effect gives rise to a marked increase of $\Delta\nu_i$ towards higher fields. The value of $\Delta\nu_i^{\text{max}} - \Delta\nu_i^{\text{min}}$, $\Delta\nu_{ij}$ is usually zero for complexes with T_d symmetry, and increases rapidly as the symmetry of the copper atom decreases.

For example, for the $\sim C_{3v}$ complex $(\text{PPh}_3)_3\text{CuX}$, $\Delta\nu_{ij}$ is of the order of 0-30Hz, with $\langle\Delta\nu_i\rangle \sim 900\text{Hz}$. For $\sim C_{2v}$ complexes $(\text{PPh}_3)_2\text{CuX}$, $\Delta\nu_{ij} \sim 400\text{Hz}$, $\Delta\nu_i \sim 900-1300\text{Hz}$. In the 'cubane' and 'step' configurations of $[\text{PPh}_3\text{CuX}]_4$ $\Delta\nu_{ij} \sim 300\text{Hz}$, $\Delta\nu_i \sim 1400-1700\text{Hz}$.

References:

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3. P.F. Barron, J.C. Dyason, L.M. Engelhardt, P.C. Healy and A.H. White. Aust. J. Chem. 1985, 36, 261.

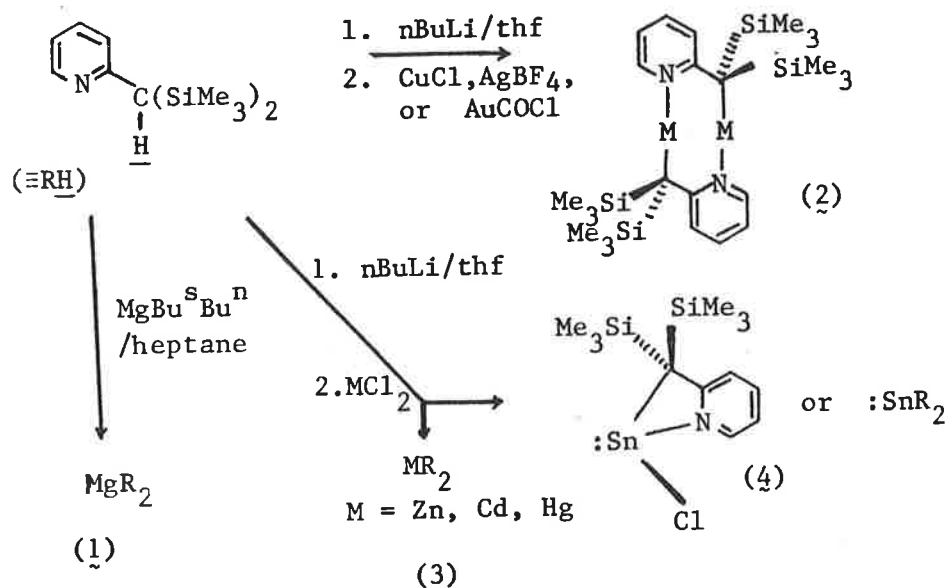
Aspects of N-Functionalized Alkyl Metal Chemistry

Mark J. Hendersen, Brian Jolly, Rocco I. Papasergio, Colin L. Raston, and Allan H. White.

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A., 6009.

The sterically hindered nitrogen functionalized alkyl ligand 2-(Me_3Si) $_2\text{CC}_5\text{H}_4\text{N}$ ($=\bar{\text{R}}$) promises to have a rich organometallic chemistry. Lithiation of RH in thf ($=$ tetrahydrofuran) yields solvated ' LiR ' which is a versatile transfer agent of $\bar{\text{R}}$. MgR_2 , (1), prepared by metallation of RH using the relatively new reagent $\text{MgBu}^{\text{S}}\text{Bu}^{\text{N}}$ (in heptane) should also prove to be a valuable precursor to other metal derivatives of $\bar{\text{R}}$, particularly where the reducing prowess of lithium reagents is a problem.

For the group I transition metals novel binuclear compounds, (2), in which the ligand is bridging two metal centres are accessible. They have remarkable thermal stability, e.g. (2), $\text{M} = \text{Cu}$ is sublimable in vacuo at 160°C^1 . The group II complexes, MR_2 , (3), are monomeric with varying degrees of interaction of the nitrogen group with the metal centre, in accordance with the changes in hard/soft character within the group. Other chemistry defined for ligand $\bar{\text{R}}$ includes the synthesis of the first stable alkylchlorostannene, (4), and dialkylstannene, $[\text{:SnR}_2]$.



THE INFLUENCE OF CONFORMATIONAL STEREOCHEMISTRY ON METAL ION CAGE PROPERTIES AND REACTIVITIES:
THE "1*le*₃" AND "ob₃" DIASTEREOMERS OF THE EICOSANE CAGE SYSTEM

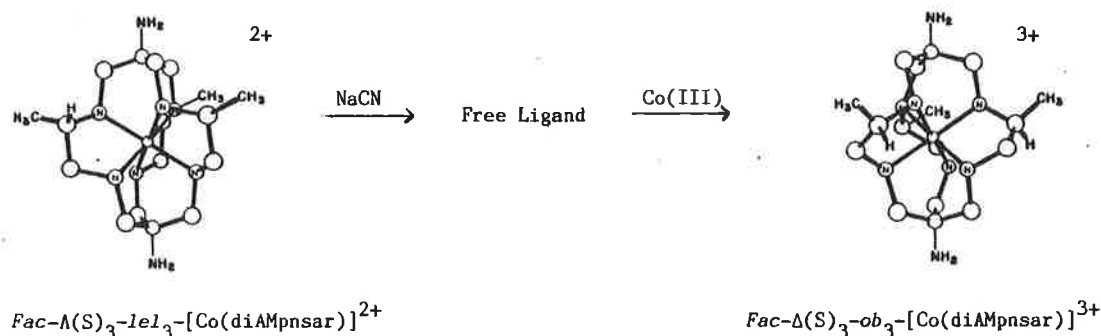
A.J. (Tony) Hendry, Rodney J. Geue and Alan M. Sargeson

Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601

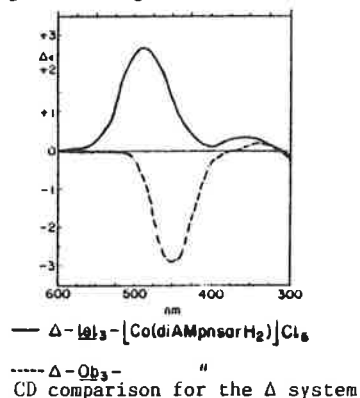
The $\sim 10^5$ -fold increase in cobalt(II,III) electron self-exchange rate achieved merely by encapsulating the $[\text{Co(en)}]^{3+}$ complex ($k_{\text{et}} = 3.4 \times 10^{-5}$) to give the $[\text{Co(diAMsar)}]^{3+}$ cage complex ($k_{\text{et}} = 0.5$), hints at an overall preferred cavity size influence on electron transfer reactions. This has also been simulated by a potential energy surface analysis of the reaction.¹ Cage systems with preferred or fixed conformations have since become an important synthetic objective in order to determine the ways in which stereochemistry can modulate such effects.

While both the "1*le*₃" diastereomers of the $[\text{Co(pn)}_3]^{3+}$ (pn = 1,2-propanediamine, all R or S), and $[\text{Co(chxn)}_3]^{3+}$ (chxn = *trans*-1,2-cyclohexanediamine, all (R,R) or (S,S)) complexes, have yielded metal ion cage molecules on reaction with nitromethane and formaldehyde,^{2,3} their "ob₃" diastereomers do not cap under similar conditions. Furthermore, although the racemization of $[\text{Co(II)(diAMsar)}]^{2+}$, i.e., inversion of Δ/Λ , has recently been achieved, attempts to find any ob₃- $\Delta(S)_3$ - $[\text{Co(diAMPnsar)}]^{3+}$ cage from the similar treatment of the *fac*- and *mer*- $\Lambda(S)_3$ -1*le*₃ forms have not yet been successful.

The *fac*- and *mer*-ob₃ diastereomers have recently been synthesized by the insertion of Co(III), via the labile *trans*- $[\text{Co(py)}_4\text{Cl}_2]^+$ complex, into the empty chiral diAMPnsar ligands. These were obtained by a cyanide induced extrusion of Co(II) from the chiral 1*le*₃ cage complexes.



Unlike the 1*le*₃ and ob₃- $[\text{Co(pn)}_3]^{3+}$ complexes, which have similar characteristics, the 1*le*₃ and ob₃ cages show some remarkable differences, both from each other and from their analogous $[\text{Co(pn)}_3]^{3+}$ substrates. For example, the 1*le*₃ isomer has a typical orange colour in the visible region ($^1A_{1g} \rightarrow ^1T_{1g}$; $\epsilon(\text{max})_{480\text{nm}} = 140 \text{ M}^{-1}\text{cm}^{-1}$), while the ob₃ form is yellow-green ($^1A_{1g} \rightarrow ^1T_{1g}$; $\epsilon(\text{max})_{453\text{nm}} = 93 \text{ M}^{-1}\text{cm}^{-1}$), with the ligand field approaching the strongest known for a saturated Co(III) N_6 chromophore. This is indicative of the compressed nature of the ob₃ cavity about the metal ion. Their chiroptical properties are also remarkably different, with the CD spectra being of opposite sign and similar magnitudes for the same chelate ring configuration. Comparisons of their structural, spectral, electrochemical and electron self-exchange properties will be presented, together with some preliminary results of complete energy surface modelling of the electron self-exchange barriers.



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3. R.J. Geue and A.J. Hendry, unpublished work.

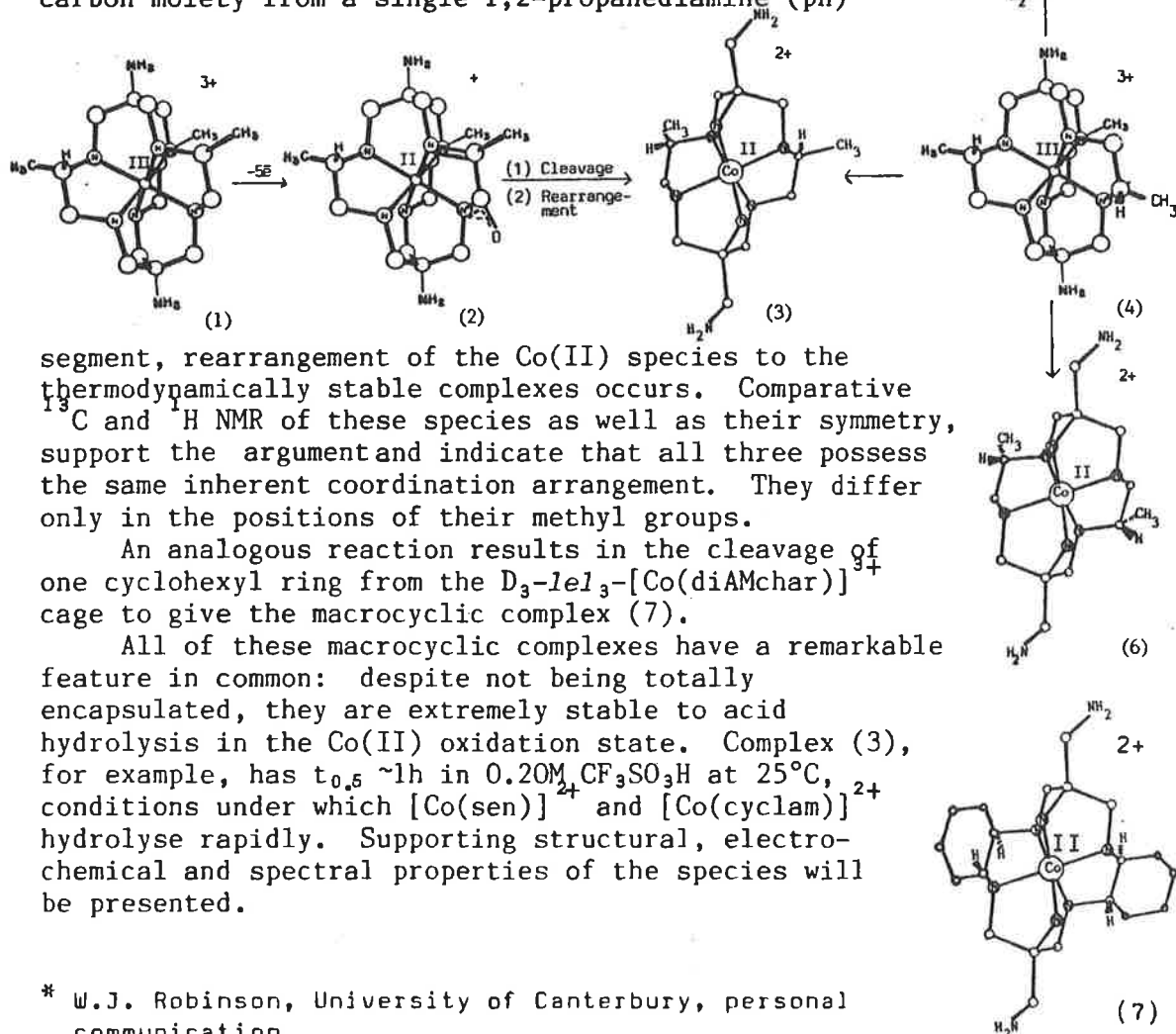
**KINETICALLY STABLE CHIRAL COBALT(II) TETRAAMINO-TETRAAZAMACROCYCLES
FROM THE OXIDATIVE DEHYDROGENATION OF ALKYLATED CHIRAL COBALT(III)
CAGE SYSTEMS: ASYMMETRIC MACROCYCLE SYNTHESIS**

A.J. (Tony) Hendry, Rodney J. Geue and Alan M. Sargeson

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Three chiral Co(II) tetraamino-tetraazamacrocycles have been identified from high temperature anoxic treatment of *fac*- and *mer*- $\Lambda(S)_3$ -[Co(diAMPnsar)]³⁺ (*lel*₃) cages in basic solution. As shown in the scheme, the *mer-lel*₃ cage (4) gives three macrocycles, (3), (5) and (6), one of which is identical to the single product (3) derived from the *fac-lel*₃ cage (1). A crystal structure* identified this species as the Co(III) complex of (3).

Both an imine and an imine-amide complex (2) have been identified from incomplete reactions. The hydrolytic cleavage of this function in the *fac-lel*₃ cage, with C₃ symmetry, could result only in a single product, whereas the *mer-lel*₃ cage, with C₁ symmetry, gives three possibilities. After the loss of the three-carbon moiety from a single 1,2-propanediamine (pn)



segment, rearrangement of the Co(II) species to the thermodynamically stable complexes occurs. Comparative ¹³C and ¹H NMR of these species as well as their symmetry, support the argument and indicate that all three possess the same inherent coordination arrangement. They differ only in the positions of their methyl groups.

An analogous reaction results in the cleavage of one cyclohexyl ring from the D₃-*lel*₃-[Co(diAMchar)]³⁺ cage to give the macrocyclic complex (7).

All of these macrocyclic complexes have a remarkable feature in common: despite not being totally encapsulated, they are extremely stable to acid hydrolysis in the Co(II) oxidation state. Complex (3), for example, has *t*_{0.5} ~1h in 0.20M CF₃SO₃H at 25°C, conditions under which [Co(sen)]²⁺ and [Co(cyclam)]²⁺ hydrolyse rapidly. Supporting structural, electrochemical and spectral properties of the species will be presented.

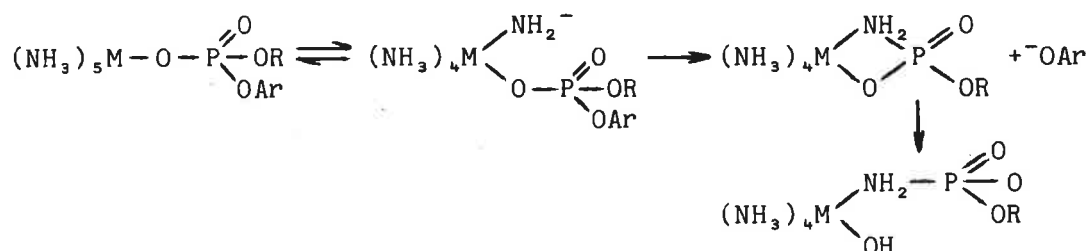
* W.J. Robinson, University of Canterbury, personal communication.

Intramolecular Reactions of Coordinated Phosphate Esters.

Philip Hendry and Alan M. Sargeson.

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G.P.O. Box 4, Canberra, A.C.T. 2601.

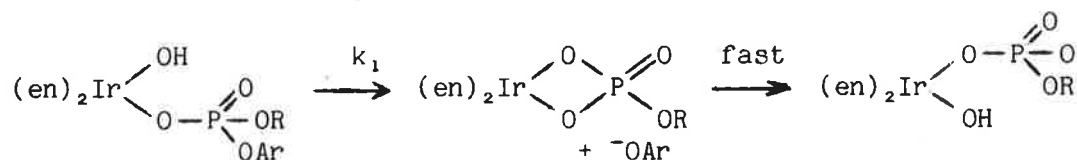
The intramolecular reactions of a series of phosphate esters coordinated to the $[(\text{NH}_3)_5\text{M}]^{3+}$ moiety ($\text{M} = \text{Co}$ and Ir) have been studied as part of an investigation into the effects that metal ions exert on the reactivity of phosphate derivatives.



- 1, $\text{M} = \text{Co}$, $\text{R} = ^-$, $\text{Ar} = \text{C}_6\text{H}_3(\text{NO}_2)_2$; $v = 2 \times 10^{-2} [\text{OH}^-][\text{complex}]$
- 2, $\text{M} = \text{Co}$, $\text{R} = \text{C}_2\text{H}_5$, $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2$; $v = 2 \times 10^{-1} [\text{OH}^-][\text{complex}]$
- 3, $\text{M} = \text{Co}$, $\text{R} = \text{Co}(\text{NH}_3)_5$, $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2$; $v = 4 \times 10^{-2} [\text{OH}^-][\text{complex}]$
- 4, $\text{M} = \text{Ir}$, $\text{R} = \text{C}_2\text{H}_5$, $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2$;
 $v = (2 \times 10^{-4} + 2 \times 10^{-4} [\text{OH}^-])([\text{OH}^-][\text{complex}])$
- 5, $\text{M} = \text{Ir}$, $\text{R} = \text{C}_6\text{H}_4\text{NO}_2$, $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2$;
 $v = (4 \times 10^{-3} + 10^{-2} [\text{OH}^-])([\text{OH}^-][\text{complex}])$. (All at 25°C)

The 4-membered ring chelate was only observed (by ^{31}P NMR) for complexes 1 and 2.

The intramolecular attack of hydroxide ion on coordinated phosphate esters about the $\text{Ir}(\text{III})$ moiety has been also followed; the reactions do not yield the chelate phosphate (ester) as a stable product, rather the initial product was the ring opened species. The initial ring closing reactions proceed $\sim 10^3$ fold slower than would be expected by comparison with the corresponding $\text{Co}(\text{III})$ reactions.



- 6, $\text{R} = \text{C}_2\text{H}_5$, $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2$; $k_1 = 4.6 \times 10^{-5} \text{ s}^{-1}$
- 7, $\text{R} = \text{C}_6\text{H}_4\text{NO}_2$, $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2$; $k_1 = 4 \times 10^{-4} \text{ s}^{-1}$
- 8, $\text{R} = ^-$, $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2$; $k_1 = 2 \times 10^{-6} \text{ s}^{-1}$

The reasons for the differences in the intramolecular reactions of the $\text{Co}(\text{III})$ and $\text{Ir}(\text{III})$ complexes has been attributed to the difference in the size of the two ions; $\text{Co}(\text{III})$ 0.55Å and $\text{Ir}(\text{III})$ 0.68Å. The larger $\text{Ir}(\text{III})$ ion should increase the energy required to form the strained 4-membered ring.

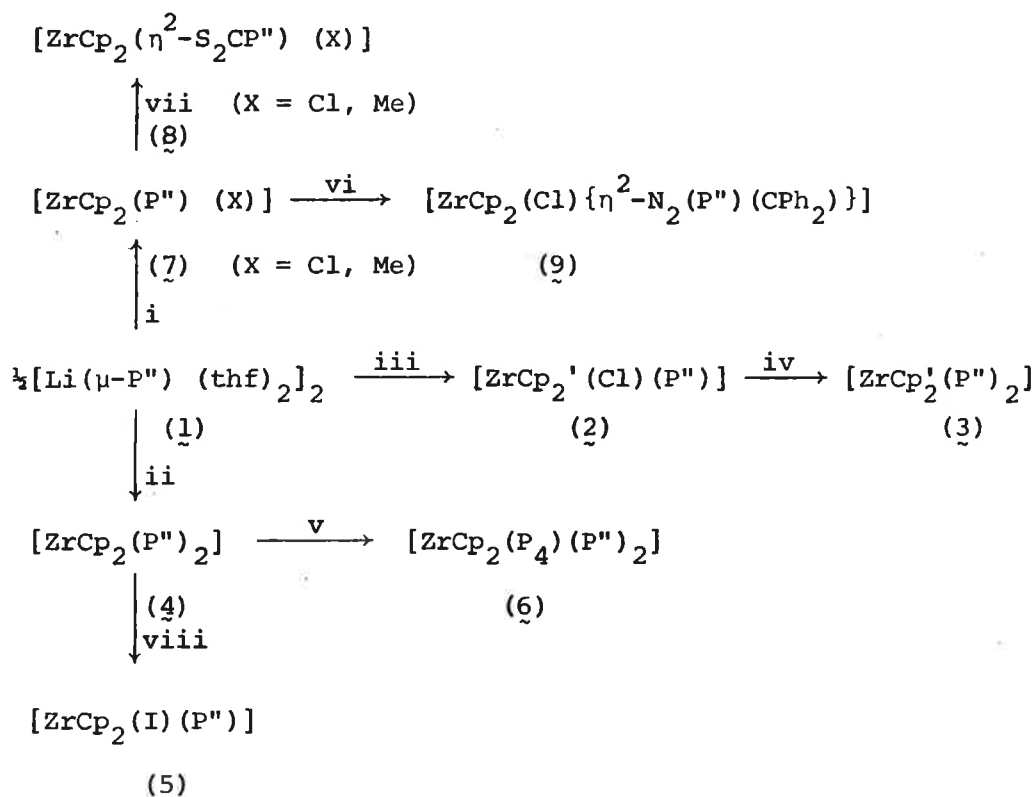
The implications of this work for the enzymic reactions of phosphate derivatives will be discussed.

Zirconocene(IV)phosphido Complexes and Some Derivatives

Dr. Evamarie Hey and Prof. Dr. Michael F. Lappert,
University of Sussex.

Present address: Dept. of Physical and Inorganic Chemistry,
University of Western Australia.

The poster will deal with a new group of zirconocene(IV)phosphido complexes, such as $[\text{ZrCp}_2(\text{P}'')(\text{X})]$ [$\text{P}'' = \text{P}(\text{SiMe}_3)_2$, $\text{X} = \text{Cl}, \text{Me}, \text{P}''$] and $[\text{ZrCp}'_2(\text{P}'')(\text{X})]$ [$\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$, $\text{X} = \text{Cl}, \text{P}''$]. Structural and spectroscopic data suggest a terminal $\text{Zr} \cdots \text{P}$ multiple bond. Reactions with heterocumulenes, diazo compounds and white phosphorus lead to insertion into the $\text{Zr}-\text{P}$ bond while Lewis bases or acids lead mainly to cleavage of the $\text{Zr}-\text{P}$ bond.



Reagents: i: $1[\text{ZrCp}_2\text{Cl}_2]$ or $1[\text{ZrCp}_2(\text{Cl})(\text{Me})]$, ii: $\frac{1}{2}[\text{ZrCp}_2\text{Cl}_2]$,
iii: $1[\text{ZrCp}_2'\text{Cl}_2]$, iv: $\frac{1}{2}[\text{Li}(\mu\text{-P}'')(\text{thf})_2]_2$, v: white
phosphorus, vi: $1\text{N}_2\text{CPh}_2$, vii: 1CS_2 , viii: 1MeI .

X-ray Structures: (1) by P.B. Hitchcock
(6)-(9) by S.G. Bott and J.L. Atwood.

Systematic Investigation of Unexpected Oxidation Processes for Mercury(II) Dithiocarbamate Complexes at Platinum and Mercury Electrodes :
Electrochemical Synthesis and Structural Characterization of
catena-{Octakis[μ -(N,N-diethyldithiocarbamato-S,S')pentamercury(II)]}
Perchlorate, $[\text{Hg}_5(\text{Et}_2\text{dtc})_8](\text{ClO}_4)_2$.

A.M. Bond¹, R. Colton², A.F. Hollenkamp¹, B.F. Hoskins², K. McGregor²,
J.E. Moir¹.

Contribution from: (1) The Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds, Victoria 3217 and (2) Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052.

The importance of internal redox reactions that follow oxidation of metal dithiocarbamates has been investigated with a detailed study of the electrochemical oxidation of mercury(II) diethyldithiocarbamate, $\text{Hg}(\text{Et}_2\text{dtc})_2$, at mercury and platinum electrodes. At both electrodes controlled potential electrolysis experiments in CH_2Cl_2 lead to the isolation of the unexpected product $[\text{Hg}_5(\text{Et}_2\text{dtc})_8](\text{ClO}_4)_2$. The yellow plate-like crystals of this complex have been characterized by X-ray structural analysis which shows alternating layers of cations and anions. The cationic layers consist of linear polymeric chains which are generated by the repetition of two $\text{Hg}_2^{1/2}(\text{Et}_2\text{dtc})_4$ units related by a centre of symmetry, one of which defines the asymmetric unit. Of the three unique mercury atoms one has an octahedral environment and is situated at a centre of symmetry, whilst the remainder have an approximately tetrahedral inner coordination environment. The dithiocarbamate ligands, which exhibit a variety of bridging modes, link the mercury atoms in a complex fashion with the result that simple bidentate coordination is absent. The Hg-S distances are 2.4 to 2.9 Å for tetrahedral mercury and for octahedral mercury there are two short (2.39 Å) and four long (2.92 - 3.22 Å) bonds.

At mercury electrodes this product is derived from the reaction: $\text{Hg} + 2\text{Hg}(\text{Et}_2\text{dtc})_2 \rightarrow [\text{Hg}_3(\text{Et}_2\text{dtc})_4]^{2+} + 2\text{e}^-$. This species is in equilibrium with other Hg- Et_2dtc species with $[\text{Hg}_5(\text{Et}_2\text{dtc})_8](\text{ClO}_4)_2$ being the least soluble. At a platinum electrode a mercury(III) - containing species is implicated: $\text{Hg}(\text{Et}_2\text{dtc})_2 \rightarrow [\text{Hg}(\text{Et}_2\text{dtc})_2]^+ + \text{e}^-$; $2[\text{Hg}(\text{Et}_2\text{dtc})_2]^+ + \text{Hg}(\text{Et}_2\text{dtc})_2 \rightarrow [\text{Hg}_3(\text{Et}_2\text{dtc})_4]^{2+} + (\text{Et}_2\text{dtc})_2$. Thus an authentic sample of $[\text{Hg}_5(\text{Et}_2\text{dtc})_8](\text{ClO}_4)_2$ in solution is in equilibrium with other Hg- Et_2dtc species: $[\text{Hg}_5(\text{Et}_2\text{dtc})_8]^{2+} \rightleftharpoons [\text{Hg}_3(\text{Et}_2\text{dtc})_4]^{2+} + 2\text{Hg}(\text{Et}_2\text{dtc})_2$. Reactions have been characterized by NMR, IR and UV spectroscopy, conductivity measurements, and by voltammetry at platinum and mercury electrodes. Concepts outlined in this work are believed to be generally applicable to other oxidation processes where ligands can be oxidized at less positive potentials than the coordinated metal.

ELECTROPHILIC ADDITION TO σ -ACETYLIDE COMPLEXES: SYNTHESIS AND STRUCTURE OF SOME ARYLDIAZO-, CYCLOHEPTATRIENYL- AND HALO-VINYLDIENE COMPLEXES.

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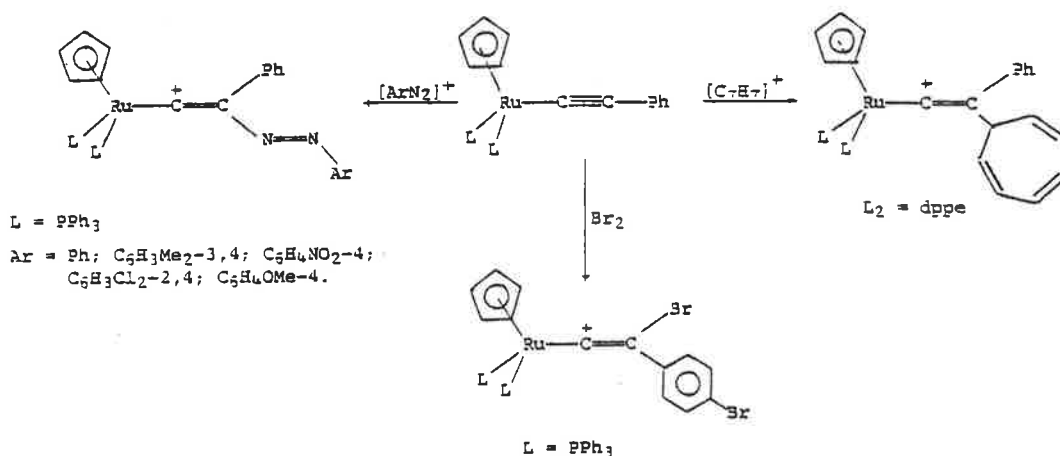
and B.K. Nicholson

Department of Chemistry, University of Waikato, Hamilton, New Zealand

Experimental and theoretical studies have shown that the β carbon in transition metal acetylide complexes is electron rich and will react with electrophilic reagents such as H^+ , Me^+ and Et^+ .^{1,2}

The range of known vinylidene ligands has been extended. Arene-diazonium, $[ArN_2]BF_4$, and tropylium salts $[C_7H_7]PF_6$, react with THF solutions of $Ru(C_2Ph)(L_2)(\eta-C_5H_5)$ [$L_2 = (PPh_3)_2$ or dppe] affording the corresponding aryldiazovinyldiene complexes, $[Ru(C=CPhN=NAr)(PPh_3)_2(\eta-C_5H_5)][BF_4]$, and cycloheptatrienyl vinylidene complex, $[Ru(C=CPh-C_7H_7)(dppe)(\eta-C_5H_5)]PF_6$.

This characteristic reactivity of electrophiles also extends to the halogens, Cl_2 , Br_2 and I_2 . Excess bromine reacts with $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ to give a quantitative yield of $[Ru\{C=CBBr(C_6H_4Br-4)\}(PPh_3)_2(\eta-C_5H_5)]Br_3$. The structures of all three types of complexes have been established by X-ray structural studies.



The reactivity of these vinylidenes has been examined. The aryldiazo- and cycloheptatrienyl vinylidenes react with MeO^- to regenerate the σ -acetylide, with $MeOH$ to form $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta-C_5H_5)]^+$, and with H_2O to form $[Ru(CO)(PPh_3)_2(\eta-C_5H_5)]^+$. The bromo-vinylidene reacts with K-Selectride and with MeO^- to form $Ru(C\equiv CC_6H_4Br-4)(PPh_3)_2(\eta-C_5H_5)$.

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2. N.M. Kostic and R. Fenske, *Organometallics*, 1982, **1**, 974.

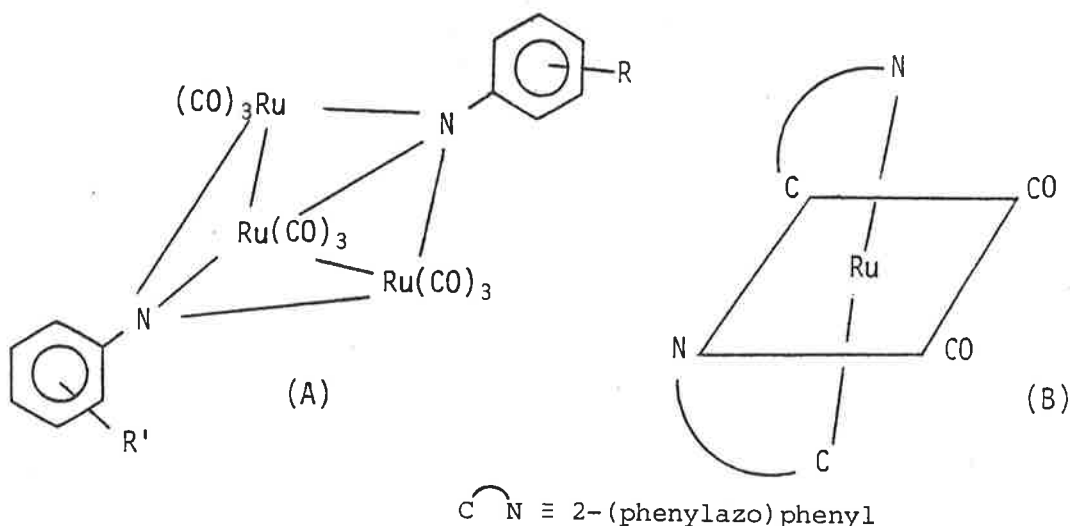
SYNTHESIS, STRUCTURE AND REACTIVITY OF BIS(ARYLIMIDO)TRIRUTHENIUM CLUSTERS $[\text{Ru}_3(\mu_3\text{-NR})_2(\text{CO})_9]$

Michael I. Bruce, Mark G. Humphrey, Omar bin Shawkataly, Michael R. Snow and Edward R.T. Tiekink

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001.

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with azobenzene leads to the formation of $\text{Ru}_3(\text{CO})_9(\mu_3\text{-NPh})_2$. The 2 NPh groups each act as 4 electron donors, capping both sides of the cluster. The same complex has been isolated from reactions between $\text{Ru}_3(\text{CO})_{12}$ and nitrobenzene, and fully characterised by an X-ray structural determination.¹

The use of substituted azobenzenes $\text{RC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{R}'$ ($\text{R} = \text{H}$, $\text{R}' = m\text{-F}$, $p\text{-F}$, $o\text{-F}$, $m\text{-CH}_3$, $m\text{-CF}_3$, $o\text{-Br}$; $\text{R} = \text{R}' = \text{H}$, $m\text{-CH}_3$, OMe) results in the related compounds (A).



A minor product from the reaction is the mononuclear complex $\text{Ru}(\text{CO})_2(\text{azb})_2$ [azb = 2-(phenylazo)phenyl] shown to be isomer (B) by a single-crystal X-ray structure determination.

The reactions of the parent compound, $\text{R} = \text{R}' = \text{H}$ with simple 2-e donor ligands such as CO , PR_3 , $\text{P}(\text{OR})_3$, CNR , AsR_3 , $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ ($n = 1, 2$) and with small organic molecules such as C_2H_4 , C_2H_2 , $\text{C}_2(\text{CN})_4$, HC_2Ph , C_2Ph_2 and $\text{C}_2(\text{CO}_2\text{Me})_2$ will be reported.

Reference

1. W. Clegg, G.M. Sheldrick, D. Stalke, S. Bhaduri and K.S. Gopalkrishnan, *Acta Cryst.*, (1984) C40, 927-929.

SOME CHEMISTRY OF PENTAKIS(METHOXYCARBONYL)CYCLOPENTADIENE - OXYGEN AND CARBON INTERACTIONS WITH METALS

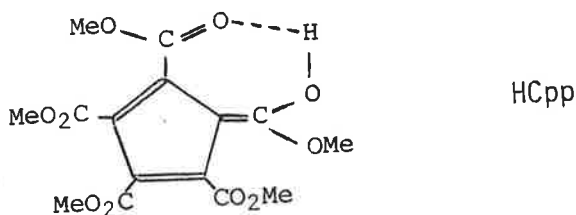
Michael I. Bruce, Paul A. Humphrey

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001.

Brian W. Skelton and Allan H. White

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009.

We have investigated the metal chemistry of pentakis(methoxycarbonyl)cyclopentadiene, $\text{HC}_5(\text{CO}_2\text{Me})_5$ or HCcpp, a strong organic acid. The solid state structure of HCcpp corresponds to the hydroxy-fulvene arrangement with the acidic hydrogen asymmetrically bridging two carbonyl oxygens. The metal ion is similarly *O*-coordinated in its alkali-metal, alkaline-earth-metal, cadmium, thallium and first-row transition-metal compounds. Metal-ring carbon interactions have been found in a number of complexes of silver(I) and gold(I) though not in copper(I) complexes.¹



Ruthenium complexes show η^5 -bonding of the Cpp ligand in $\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{-}\{\eta\text{-C}_5(\text{CO}_2\text{Me})_5\}$, while in other complexes such as $(\text{CH}_3\text{COO})\text{Ru}(\text{PPh}_3)_2\text{Cpp}$ and $(\text{CH}_3\text{COO})_2\text{Ru}_2(\text{PPh}_3)_2(\text{Cpp})_2$ there is bonding through the carbonyl oxygens to the metal. The latter two are the first compounds we have synthesized in which the covalent nature of the bonding is still present in solution; the Cpp ligand does not dissociate as an anion.

A number of complexes have been prepared by reacting TlCpp with halogen-bridged rhodium compounds. $(\text{COD})\text{RhCpp}$ exhibits a η^5 interaction between the Cpp and the metal, while $(\text{azb})_2\text{RhCpp}$ has coordination through oxygens which remains intact in solution as in the ruthenium examples. The reaction between $[(\text{CO})_2\text{RhCl}]_2$ and TlCpp has given an unusual product postulated to be $\text{Rh}\{\eta^4\text{-C}_5\text{H}_4(\text{CO}_2\text{Me})_2\}\{\eta^5\text{-C}_5\text{H}(\text{CO}_2\text{Me})_4\}$. The loss of CO_2Me groups may be due to steric interactions between the CO_2Me groups in the two rings. Addition of dppe to $(\text{COD})\text{RhCpp}$ has resulted in the retention of both COD and Cpp.

Reference

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Structural and Electronic Consequences of Coordinating
Butadienes to CpMo(NO) .

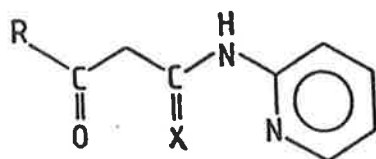
N.J. Christensen, A.D. Hunter and P. Legzdins*. Dept. of Chemistry, University of British Columbia, Vancouver, B.C., Canada. F.W.B. Einstein* and A.C. Willis. Dept. of Chemistry, Simon Fraser University, Burnaby, B.C., Canada. B.E. Bursten* and M.G. Gatter. Dept. of Chemistry, Ohio State University, Columbus, Ohio, USA.

The synthesis of the novel complexes $\text{CpMo(NO)}(\eta^4\text{-trans-diene})$ (diene=acyclic conjugated diene) and $\text{CpMo(NO)}(\eta^4\text{-cis-2,3-dimethylbutadiene})$ are reported. These complexes are preparable in moderate yields by the reduction of $(\text{CpMo(NO)I}_2)_2$ with sodium amalgam in THF in the presence of the appropriate diene. A mechanism for these reduction reactions is proposed. These complexes have been fully characterized by conventional spectroscopic techniques, single-crystal X-Ray crystallographic analyses, and Fenske-Hall Molecular orbital calculations. The cis-diene complexes are the kinetic products of these reduction reactions. They irreversibly isomerize to give the thermodynamically preferred trans complexes in solution. The origin of this unprecedented selectivity for trans-diene coordination will be described.

SYNTHESIS, STRUCTURES AND MAGNETISM OF CHELATED
METAL AMIDE AND THIOAMIDE COMPLEXES

P. Iliopoulos, G.D. Fallon and K.S. Murray

The coordinating properties of the binucleating ligands LH are being studied.

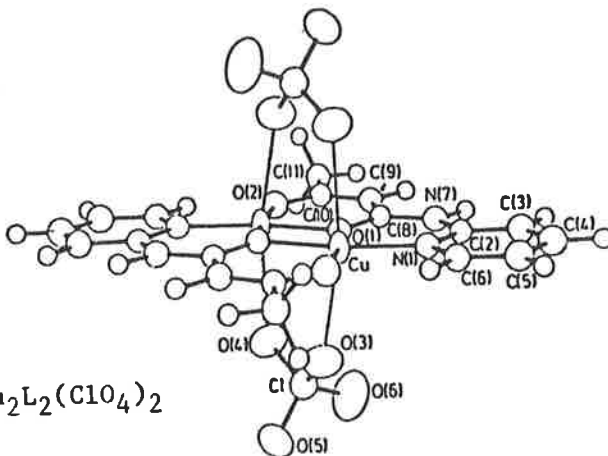


LH

X = O, S

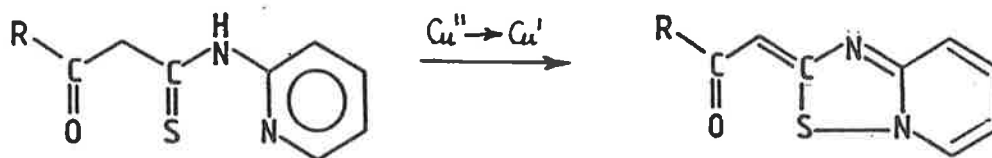
R = Me, Ph

$\text{Cu}_2\text{L}_2(\text{ClO}_4)_2$



The amide (X = O) ligands readily coordinate with Cu^{II} , yielding both mononuclear and binuclear complexes of types CuL_2 and $\text{Cu}_2\text{L}_2\text{X}_2$ (X = ClO_4^- , NO_3^- , RSO_2^-). In a structurally characterized binuclear complex the counter anions (ClO_4^-) have been found to bridge the metal ions but show little contribution to the strength of coupling.¹ The R = Me amide readily condenses with diamines ($\text{H}_2\text{N}(\text{CH}_2)_x\text{NH}_2$, X = 2,3,4) forming Schiff bases which readily coordinate with Cu^{II} to form mononuclear complexes.

The thioamide (X = S) ligands show interesting coordination and redox properties. At RT, complexes of the type ML_2 have been obtained for Ni^{II} and Zn^{II} , whereas oxidation of the ligand occurs in the presence of Cu^{II} .



1. Iliopoulos, P., Fallon, G.D. and Murray, K.S., J. Chem. Soc., Dalton Trans., in press.

REACTIONS OF URETHANE AND PHENYLUREA COORDINATED TO
PENTAAMMINECOBALT(III)

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Department of Chemistry,
University of New South Wales,
Duntroon, Canberra ACT 2600.

Linkage isomeric nitrogen and oxygen bonded pentaamminecobalt(III) complexes have been synthesized for the ambidentate ligands urethane ($\text{NH}_2\text{CO}_2\text{CH}_2\text{CH}_3$) and phenylurea ($\text{NH}_2\text{CONHC}_6\text{H}_5$). The protonated N-isomers rapidly rearrange to the O- forms in solution, by an intramolecular pathway. Also, activation of the ligands by coordination through nitrogen is evidenced by the observation of significant C-N cleavage. The urethane and urea complexes both yield $\text{Co}(\text{NH}_3)_6^{3+}$, but by different routes. In neither case is the N-carbamate complex $(\text{NH}_3)_5\text{CoNH}_2\text{CO}_2^{2+}$ involved, although this was a clear possibility and this ion is known to decay rapidly to the hexaammine in acid. It is shown that the phenylurea species entails exo C-N cleavage in the first step, resulting in aniline and the N-cyanate species $(\text{NH}_3)_5\text{CoNCO}^{2+}$ by an elimination process. This mode of metal ion promoted degradation of an urea is novel, and may relate to the enzymic reaction (Ni(II) urease).

The O-bonded isomers undergo primarily substitution at the metal centre, in both acid and base hydrolysis, and there is some competitive O- to N- linkage isomerization.

The mechanisms of these and related reactions are considered.

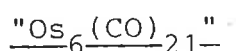
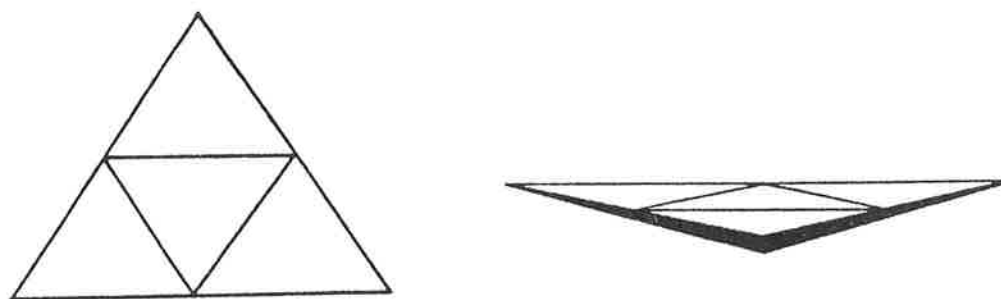
Reaction of Small Molecules on Hexaosmium 'Raft' Carbonyl Clusters
 C. Hay^a, J.G. Jeffrey^b, B.F.G. Johnson^a, J. Lewis^a, R.R. Raithby^a,
 and D.A. Welch^c.

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(b) *Department of Chemistry, The University of Auckland.*

(c) *Chemistry Department, Edinburgh.*

Recently, synthesis of the hexaosmium 'Raft' carbonyl cluster has been improved, enabling a systematic study on how small molecules react on such a planar metallic like surface.



The activated complex $[\text{Os}_6(\text{CO})_{20}(\text{MeCN})](1)$ readily reacts with terminal acetylenes (HC_2R , $\text{R}=\text{Ph}$, Me) to form novel vinylidene complexes, $[\text{Os}_6(\text{CO})_{20}(\text{CC}(\text{H})\text{R})](2)$. Mild thermolysis of (2) causes the cluster to contract to a pentaosmium cluster $[\text{Os}_5(\text{CO})_{15}(\text{CC}(\text{H})\text{R})](3)$.

Other small molecules, namely O_2 and S , have been reacted on the readily prepared phosphine substituted cluster $[\text{Os}_6(\text{CO})_{20}(\text{PPh}_3)](4)$ to yield the capped species $[\text{Os}_6(\text{CO})_{17}(\mu_3\text{-O})(\mu_3\text{-CO})(\text{PPh}_3)](5)$ and $[\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})](6)$ respectively. The electrochemistry behaviour of the former complex has been studied and revealed significant differences to that observed for the normal phosphite/phosphine substituted series $[\text{Os}_6(\text{CO})_{21-n}\{\text{P}(\text{R})_3\}_n]$ ($\text{R}=\text{Ph}$, $n=1\rightarrow3$, $\text{R}=\text{OMe}$, $n=1\rightarrow6$).

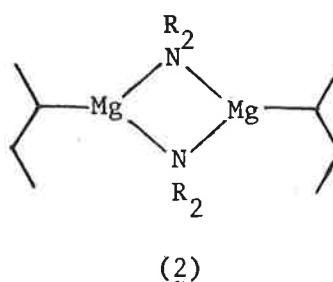
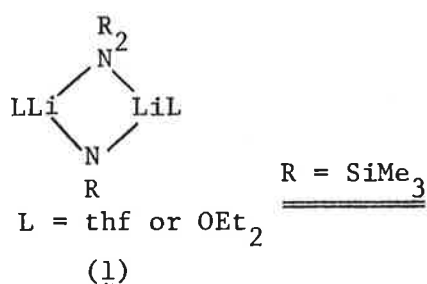
Finally another capped complex $[\text{H}_2\text{Os}_6(\text{CO})_{18}(\mu_3\text{-PPh})](7)$, has been prepared by the thermal activation of the terminally bound monoorgano-phosphine compound, $[\text{Os}_6(\text{CO})_{20}(\text{PPhH}_2)](8)$.

Lithium and Magnesium Sterically Hindered Amide and Alkoxide Complexes

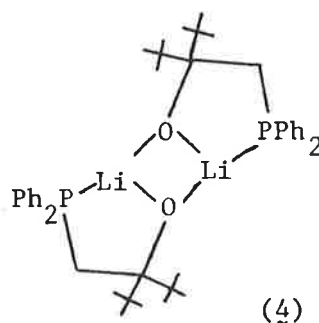
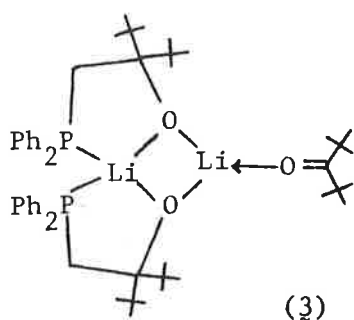
Lutz M. Engelhardt, Geraldine E. Jacobsen, Peter C. Junk, Burns H. Newton, Colin L. Raston, and Allan H. White.

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A., 6009.

Bulky ligands can affect both the state of aggregation and co-ordination environment about the metal centre in their complexes. Moreover such ligands usually contain lipophilic groups such as $-\text{Bu}^t$ and $-\text{SiMe}_3$ which tend to render the complexes hydrocarbon soluble. Treatment of $\text{HN}(\text{SiMe}_3)_2$ with $n\text{BuLi}$ in OEt_2^1 or thf, for example, yields dimeric hexane soluble amido complexes, (1), containing three coordinate metal centres. The relatively new reagent MgBu^sBu^n in heptane initially yields (2) then ' $\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2$ '. Some novel N-functionalized amido lithium complexes have also been prepared via metallation of the amines, 2-trimethylsilylamino-6-methylpyridine and 8-trimethylsilylaminoquinoline.



A new highly hindered P-functionalized alkoxide ligand has been developed. Reaction of $\text{LiCH}_2\text{PPh}(\text{tmeda})^*$ with Bu_2^tCO in hexane yields the novel ketone complex, (3) which then slowly reacts with excess ketone yielding (4). The coordinated ketone in (3) can be considered as a model 'activated ketone' for the 1,2-addition of organolithium reagents to carbonyl compounds. It is generally agreed that such addition initially involves formation of a ketone complex, but none have been properly identified.



* $\text{tmeda} = \text{N,N,N',N'}$ -tetramethylethylenediamine

1. L.M. Engelhardt, A.S. May, C.L. Raston, and A.H. White, J. Chem. Soc., Dalton Trans., 1984, 1671; M.F. Lappert, M.J. Slade, A. Singh, J.L. Atwood, R.D. Rogers and R. Shakir, J. Am. Chem. Soc., 1983, 105, 302.

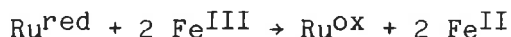
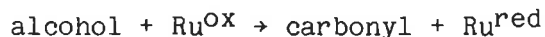
RUTHENIUM CATALYSED OXIDATION OF ALCOHOLS

Robert Kaziro and James K. Beattie

School of Chemistry, University of Sydney

There have been many studies of ruthenium catalysed oxidations of organic compounds in aqueous solution (E.S.Gore, Platinum Metals Review 1983,27,111). Different sources of ruthenium include $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, and RuO_4 . A variety of oxidants have been used, including NaOCl , NaIO_4 , $\text{K}_2\text{S}_2\text{O}_8$, O_2 , and $\text{K}_3[\text{Fe}(\text{CN})_6]$.

Our previous work has concerned the ferricyanide oxidation of alcohols in alkaline solutions catalysed by ruthenium trichloride (A.F.Godfrey & J.K.Beattie, Aust.J.Chem. 1979,32,1905 and P.Becker and J.K.Beattie, Aust.J.Chem. 1982,35,1245). These kinetics studies revealed that the reaction proceeds in two discrete steps:



Either of these steps can be made rate limiting by suitable adjustment of the reagent concentrations.

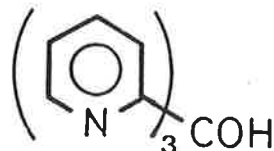
Current work has examined the pH dependence of the reaction and the identification of the oxidation states of the catalyst. The above mechanism implies that if the first step is rate limiting the rate of the reaction should be independent of the identity of the oxidant used. This has now been demonstrated. Comparison with spectrophotometric and electrochemical observations in the literature enable the oxidised form of the catalyst, Ru^{OX} , to be identified as perruthenate, RuO_4^- . The pH dependence of the reaction is explained by the precipitation of the ruthenium as $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ at pH's less than about 11. The results suggest that this mechanism is general for a wide variety of ruthenium catalysed oxidations.

MODE OF COORDINATION OF TRIS(2-PYRIDYL)CARBINOL TO COBALT(III)

F. Richard Keene and David J. Szalda

Department of Chemistry and Biochemistry, James Cook University of North Queensland; and Department of Chemistry, Brookhaven National Laboratory*, Upton, New York, U.S.A.

There have been a number of reports^{1,2,3} of complexes involving the tripodal ligand tris(2-pyridyl)carbinol:



In principle, the ligand may coordinate via the three py-N or the alcohol-O as ligating atoms. Previous reports of the bis(ligand)cobalt(III) complex are confusing as to the coordination mode. Boggess *et al.*² and White and Faller³ have both identified the complex to contain one deprotonated and one non-deprotonated ligand: the deprotonated ligand was considered to have py_3CO^- -N,N',O coordination, but the two reports differ as to the nature of the coordination mode of the non-deprotonated ligand *viz.* py_3COH -N,N',O² or py_3COH -N,N',N''.³

The present work has identified two linkage isomers of the bis-{tris(2-pyridyl)carbinol}cobalt(III) cation. A symmetrical form has now been isolated in which all donor atoms are py-N (i.e. bis(py_3COH -N,N',N'')). An unsymmetrical form (which corresponds to that obtained by previous workers) has one deprotonated ligand coordinated through two py-N atoms and the alkoxy-O (i.e. (py_3COH -N,N',N'')(py_3CO^- -N,N',O)).

The paper will present details of the synthesis (and interconversion) of the two linkage isomers, their characterization by NMR, and a crystal structure of the symmetrical form. The electrochemical properties of the two isomers will also be given.

1. A.J. Canty, N. Chaichit, B.M. Gatehouse, and E.E. George, *Inorg. Chem.*, **20**, 4293 (1981).
2. R.K. Boggess and S.J. Boberg, *J. Inorg. Nucl. Chem.*, **42**, 21 (1980).
3. D.L. White and J.W. Faller, *Inorg. Chem.*, **21**, 3119 (1982).

* Work at BNL performed under auspices of U.S.-DOE.

Hexameric Triphenylphosphine copper(I) hydride/chloride

Peter C. Healy, John D. Kildea, Colin L. Raston and Allan H. White
Griffith University and University of Western Australia.

Although the non-hydrogen atom structure of the hexameric 1:1 tri-phenylphosphine : copper(I) hydride adduct is well-known¹, the location of the hydrogen atoms in the molecular core remains enigmatic. The results of a preliminary study directed towards the resolution of these have revealed an interesting anomaly, to be the subject of further study: Synthesis of the complex by reaction of tetrakis(triphenylphosphine)copper(I) chloride) but with K selectride (rather than sodium trimethoxyborohydride) in thf (rather than dmf) yielded well formed red crystals apparently of the product, with similar unit cell dimensions. With the intention of resolving the hydrogen atoms, a carefully measured room temperature single crystal X-ray data set was obtained and refinement initiated using the original non-hydrogen atom coordinates. In the initial determination, the Cu₆ octahedron is compressed along a trigonal axis, with Cu...Cu within the trans-faces 2.63 - 2.67 Å and between these faces 2.49 - 2.60 Å. The results of our study indicated a much greater range of adjacent Cu...Cu distances (2.441(3) - 3.683 Å) with a residual in the associated difference map. Subsequent modelling and refinement of difference map artefacts suggest the hydrogen atoms to be located on four faces and two edges within the crystal under study, one edge hydrogen substantially replaced by a chlorine atom with consequent geometrical irregularity. Detailed results will be presented.

¹Churchill, M.R., Bezman, S.A., Osborn, J.A., and Wormald, J.,
Inorg. Chem., 1972, 11, 1818.

"A New Understanding of the Photochemically Active
Excited State of $\text{Ru}(\text{bpy})_3^{2+}$."

James Ferguson and Elmars Krausz*

Research School of Chemistry ,ANU
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Although interest in the photochemical activity of $\text{Ru}(\text{bpy})_3^{2+}$ has waned since the initial reports of its photo-decomposition of water, work on the underlying electronic structure and anomalies in luminescence polarization ratios has continued unabated. Central to many arguments has been the question of localization of the (metal to ligand) transferred electron. Influenced by striking excited state Raman spectra reported in solution, some workers have considered that the electron is strongly localized, and have developed rather artificially constrained models to account for excitation polarization anomalies.

We have made a number of observations that clearly refute these ideas and have developed a more comprehensive understanding of all the available data. Firstly, we have already reported that excited state Raman¹ spectra taken in solid phases are radically different to those observed in solution and secondly the luminescence spectral profile shows a time evolution² on the nanosecond timescale in viscous solutions.

Excitation polarization ratios measured in single crystals of $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2$ show no dispersion through the singlet and triplet regions, clearly refuting any idea of an "evolution" from localized to delocalized behaviour. There is however a clear gap between triplet absorption and luminescence, indicating a relaxation in the solid state as well. We have obtained further evidence that the anomaly at 20000 cm^{-1} seen in frozen glasses and plastics is due to a range of distorted sites.³

The behaviour of the luminescence below 10 K is fascinatingly complex and in some ways analagous to the change that occurs in going from solution to rigid glass. The time-resolution, temperature dependence and anisotropy in a magnetic field of the luminescence can be coherently interpreted. The luminescence is increased when the magnetic field is transverse to the C_3 axis of the complex, in marked contradiction to the prediction of other models.

The absorption process involves the three ligands equivalently. In fluid solution, the triplet excited state rapidly relaxes to a strongly localized state that gives rise to luminescence and excited state Raman spectra. In solid phases this localization process is inhibited above 10 K. Below this temperature, luminescence from a non-thermally equilibrated,⁴ long radiative lifetime state develops with a changing spectral polarization and profile. We suggest that in this state, electron localization competes with radiative decay.

1. E. Krausz, Chem.Phys.Lett., 116,501,(1985).
2. J. Ferguson, E.R. Krausz and M. Maeder, J.Phys.Chem., 89,1852,(1985).
3. J. Ferguson and E. Krausz., submitted to Inorg. Chem.
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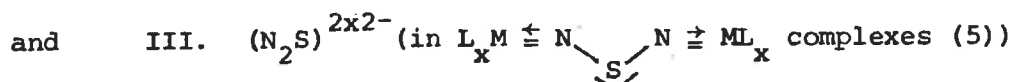
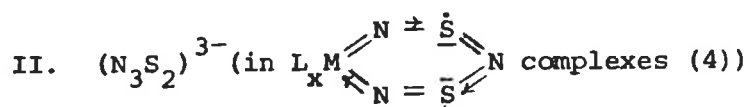
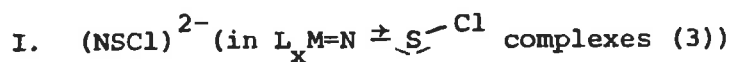
Transition Metal-Nitrogen Multiple Bonds:

New Structural and Synthetic Aspects

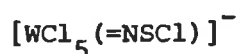
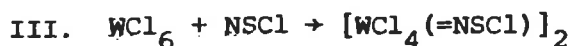
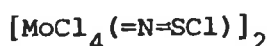
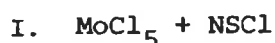
Ulrich Kynast and Kurt Dehnicke
 Philipps-Universität Marburg, 355 Marburg
 Hans Meerwein-Str. Fb Chemie, West Germany
 Present address: Dept. of Phys. and Inorg. Chem.
 University of Western Australia, Nedlands, W.A. 6009.

Many compounds containing transition metal nitrogen multiple bonds have been synthesized after the detection of $\text{Mo}(\equiv\text{N})\text{Cl}_3$ by Dehnicke in 1965 (1). Since the discovery that $(\text{NSCl})_3$ yields thionitrosyl-complexes, $\text{L}_x\text{M}=\text{N}=\ddot{\text{S}}$ (2), a variety of related systems with transition metal nitrogen bonds could be established.

Compounds containing the synthetically interesting ligands



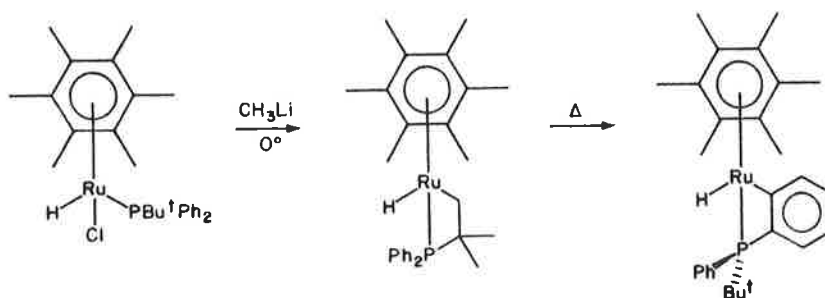
have been prepared and characterized using spectroscopic techniques and X-ray structural determination.



- (1) K. Dehnicke and J. Strähle, Z. Anorg. Allg. Chem. 339 (1965) 171, ibid 375 (1970) 238.
- (2) T.J. Greenough, B.W.S. Kolthammer, P. Legdzins and J. Trotter, Inorg. Chem. 12 (1979) 3548.
- (3) U. Kynast, U. Müller and K. Dehnicke, Z. Anorg. Allg. Chem. 508 (1984) 26.
- (4) U. Kynast, E. Conradi, U. Müller and K. Dehnicke, Z. Naturforsch. 39b (1984) 1680.
- (5) U. Kynast, W. Willing, U. Müller and K. Dehnicke, Z. Anorg. Allg. Chem. xxx (1985) in press.

CYCLOMETALLATION REACTIONS OF THE $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{PR}_3)$ FRAGMENT.MARTIN A. BENNETT AND JOZEF L. LATTENResearch School of Chemistry, Australian National University,
GPO Box 4, Canberra, ACT 2601.

Treatment of the complexes $\text{RuHCl}(\eta^6\text{-C}_6\text{Me}_6)(\text{PR}_3)$ with methyllithium results in metallation of the phosphorus ligand substituents under very mild conditions (see Figure). These reactions probably proceed by oxidative addition of substituent C-H bonds in the co-ordinatively unsaturated zero-valent ruthenium intermediate $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{PR}_3)$.



Many of these cyclometallation reactions are reversible, and kinetically and thermodynamically favoured isomers arising from metallation of unsymmetrically substituted phosphine ligands $\text{PR}_2\text{R}'$ at different sites can be observed. The main factors controlling the site of metallation appear to be:

- 1) Steric effects. Sterically demanding environments favour cyclometallation and often stabilize kinetic products.
- 2) Ruthenium-carbon bond strengths. Greater $\text{Ru-C}_{\text{aryl}}$ bond strength generally favours aryl over alkyl metallated products.
- 3) Ring strain. Three-membered rings are not observed; low ring strain favours five-membered rings over four-membered rings.

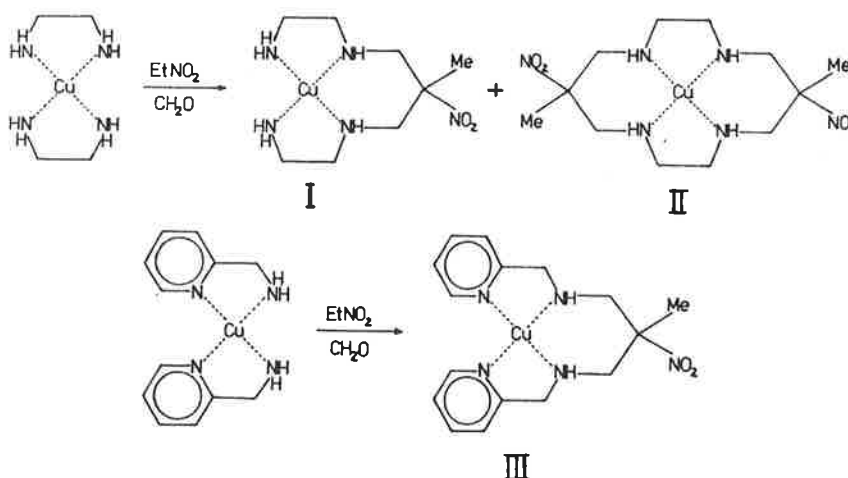
The balance between these factors determines the outcome of the cyclometallations and the poster presentation will illustrate these effects.

**TEMPLATE SYNTHESSES INVOLVING CARBON ACID CONDENSATIONS.
PREPARATION, STRUCTURE AND SPECTROSCOPY OF MULTIDENTATE
AND MACROMONOCYCLIC AMINE COPPER(II) COMPLEXES.**

P. Comba,^a N.F. Curtis,^b T.W. Hambley,^c G.A. Lawrance,^d B.W. Skelton,^e
and A.H. White^e

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- (b) Department of Chemistry, Victoria University of Wellington, New Zealand.
- (c) Department of Inorganic Chemistry, The University of Sydney, N.S.W.
- (d) Department of Chemistry, The University of Newcastle, N.S.W.
- (e) Department of Physical and Inorganic Chemistry, University of Western Australia.

While macrobicyclization reactions of inert octahedral diamines with formaldehyde and carbon acids are well known, similar reactions with relatively labile metal ions have not been studied in detail. Using the propensity of copper(II) towards four-coordination, we have developed routes to multidentate and macromonocyclic ligands employing similar reactions. Facile syntheses of a new range of multidentate amine ligands have been developed. Typical examples are:



Syntheses, some structural characterization, voltammetry and electronic and electron spin resonance spectroscopy of I-III and the nitro-group reduction products as their copper(II) complexes will be reported. Some unusual chemistry has been observed. For example, zinc/acid reduction of III leads to the pendant diamine analogue of II as the major product.

SYNTHESIS AND HYDROLYSIS KINETICS OF PENTAKIS(METHYLAMINE)-COBALT(III) COMPLEXES WITH NEUTRAL LEAVING GROUPS

Neville J. Curtis^a and Geoffrey A. Lawrance^b

- (a) Defence Research Centre Salisbury, G.P.O. Box 2151, Adelaide, S.A.
- (b) Department of Chemistry, The University of Newcastle, N.S.W.

The recent development of complexes with the labile leaving group trifluoromethanesulfonate as inorganic synthons^{1,2} has been applied to the synthesis of a series of complexes $\text{Co}(\text{NH}_2\text{CH}_3)_5\text{L}^{3+}$ (L = urea, dimethylsulfoxide, dimethylformamide, trimethylphosphate and acetonitrile). Acid aquation reactions of these complexes have been studied and activation parameters (ΔH^\ddagger , ΔS^\ddagger and ΔV^\ddagger) have been determined. Complexes with neutral leaving groups offer the opportunity of obtaining mechanistically significant ΔV^\ddagger and ΔS^\ddagger data uncomplicated by electrostrictive effects present with charged leaving groups.

Rate constants for aquation are at least 70-fold greater than values reported for the pentaammine analogues at 25°C. While activation enthalpies are similar, both activation entropies and activation volumes are more positive for the pentakis(methylamine) complexes, yet are not particularly sensitive to the choice of leaving group. A dissociative I_d type mechanism operates with a diminished role for an incoming water molecule in the dissociated transition state in the more structurally crowded pentakis(methylamine) complexes.

REFERENCES

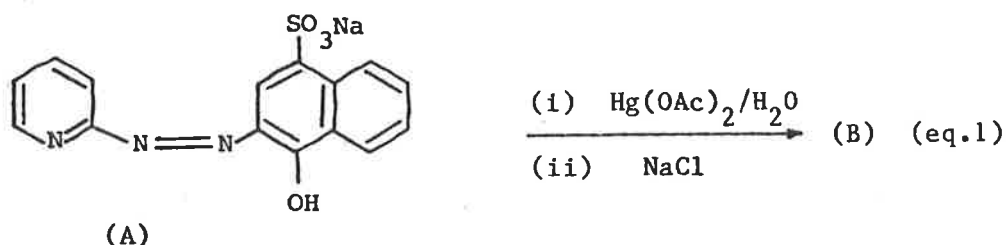
1. N.E. Dixon, G.A. Lawrance, P.A. Lay, A.M. Sargeson and H. Taube, *Inorg. Synth.*, 1985, 24, Chapter 5.
2. G.A. Lawrance, *Chem. Rev.*, 1986, 86, in press.

**INVESTIGATION OF THE MERCURATION OF SOME
2-(2'-PYRIDYLAZO)-1-NAPHTHOL-4-SULPHONATES**

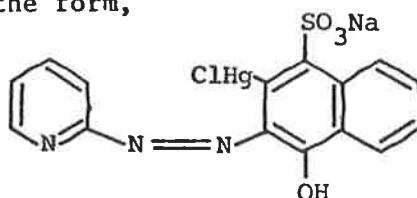
G.B. Deacon, B.M. Gatehouse, S.C. Lee, C.L. Leseberg,
P.I. MacKinnon, I.W. Stapleton and G.N. Stretton
Chemistry Department, Monash University, Clayton, Victoria, 3168.

Heterocyclic azo dyestuffs have been used as analytical reagents, especially for the complexometric and colourimetric determination of many metals, particularly in conjunction with solvent extraction procedures, e.g. Co(II), Ni(II), Pd(II), lanthanoids, etc.

Our work describes the mercuration of sodium 2-(2'-pyridylazo)-1-naphthol-4-sulphonate (α -PAN-4S), ((A), eq.1). The product, (B), has been investigated by ^1H and ^{199}Hg NMR spectroscopy.

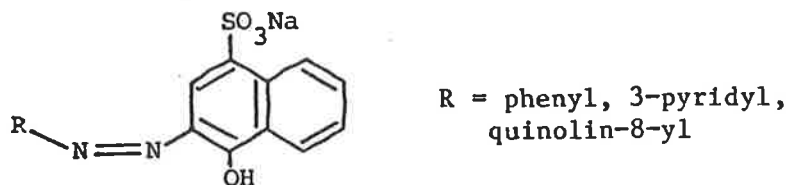


Careful analysis of the aromatic region of the ^1H NMR spectra of (A) and (B) showed the final product (B) to have one less aromatic proton compared with (A). The ^{199}Hg NMR spectrum showed a singlet (without proton decoupling) with a chemical shift consistent with an organomercurial, of the form,



and not a simple inorganic complex. However, structural assignment is incomplete due to the complexity of the ^1H NMR spectrum. A crystal structure is needed to unequivocally establish the position and mode of mercuration. Various 'large' counter-ions, e.g. Na^+ , K^+ , Cs^+ , Tl^+ , Ba^{2+} , $(\text{Bu}^t)_4\text{N}^+$, etc. have been used to crystallize a derivative suitable for X-ray determination.

There is no reaction with similar ligands of the type,



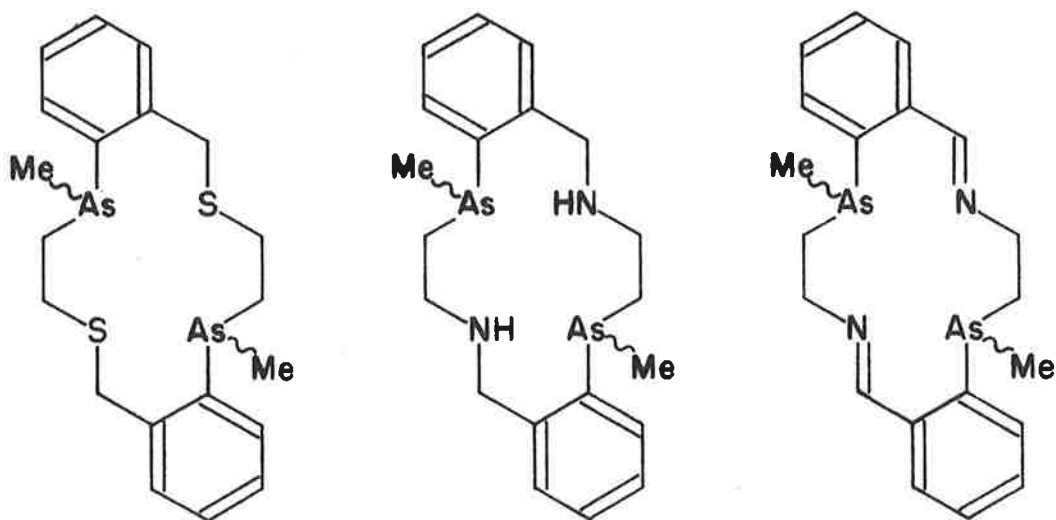
and it would thus appear that coordination of the 2-pyridyl nitrogen of (A) is essential for the mercuration to proceed.

However, prolonged standing of a solution of (B) gave single crystals. The crystal structure indicated an inorganic mercury complex with a novel five coordinate mercury.

OPTICALLY ACTIVE MACROCYCLIC LIGANDS WITH ARSENIC AND
NITROGEN OR SULFUR DONORS

Pak Hing Leung, John W.L. Martin, Gregory Organ, K.D.V. Weerasuria and
S. Bruce Wild, Research School of Chemistry, Australian National
University, Canberra, A.C.T. 2601

Details of the synthesis of a new family of optically active
macrocycles containing resolved asymmetric arsenic donors will be
presented



REACTIONS OF TRANSITION-METAL σ -ACETYLIDE COMPLEXES WITH ELECTRON-DEFICIENT OLEFINS

M.I. Bruce, T.W. Hambley, M.J. Liddell, M.R. Snow, A.G. Swincer and E.R.T. Tiekink

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001.

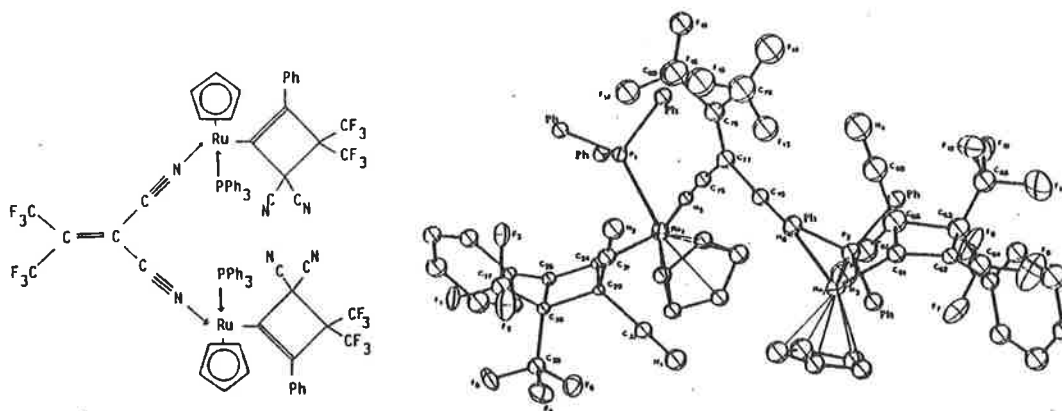
Addition of tetracyanoethylene to transition-metal σ -acetylide complexes has been shown to result¹ in the formation of

- (1) cyclobutenyl $M[C=CRC(CN)_2C(CN)_2](L)_n(\eta-C_5H_5)$
- (2) butadienyl $M[C\equiv C(CN)_2]CR\{C(CN)_2\}(L)_n(\eta-C_5H_5)$, or
- (3) "allylic" $M[\eta^3-C(CN)_2CRC=C(CN)_2](L)_n(\eta-C_5H_5)$.

complexes; for $M = W, Ru$; $L = CO, Ph_3P$; $R = Me, Ph$; $n = 1, 2, 3$.

All three structures have been characterized crystallographically. The nature of the isolated product was dependent on the reaction conditions employed. Extension of this work using the olefin 1,1-dicyano-2,2-bis(trifluoromethyl)ethene, $(NC)_2C=C(CF_3)_2$, has produced a series of cyclobutenyl complexes which ring-open to the corresponding butadienyl complexes less readily than the related tetracyanoethylene adducts. However, reaction of $Ru(C_2Ph)(Ph_3P)_2(\eta-C_5H_5)$ with the cyano-fluoro-olefin forms the binuclear complex (4) $[Ru\{C=CPhC(CF_3)_2C(CN)_2\}(Ph_3P)(\eta-C_5H_5)]_2\{\mu-(CN)_2C_2(CF_3)_2\}$ as a paramagnetic blue compound.

Structure of $[Ru\{C=CPhC(CF_3)_2C(CN)_2\}(Ph_3P)(\eta-C_5H_5)]_2\{\mu-(CN)_2C_2(CF_3)_2\}$



Work presented will include the synthesis, characterisation and reactions of several of these systems.

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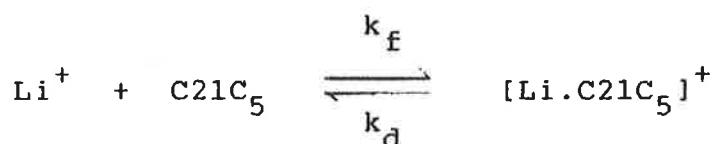
A STRUCTURAL, KINETIC AND EQUILIBRIUM STUDY OF THE
COMPLEXATION OF THE LITHIUM ION BY THE CRYPTAND 4,7,13-
TRIOXA-1,10-DIAZABICYCLO[8.5.5]EICOSANE (C21C₅).

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Sydney, New South Wales 2006.

The structure of the lithium cryptate formed with the
title cryptand, [Li.C21C₅]NCS, has been determined by
single crystal X-ray diffraction techniques. The cryptate
exists in the inclusive form in which the lithium ion
resides in the cavity formed by C21C₅ and is within
bonding distances of the two nitrogens and the three
oxygens of C21C₅. ⁷Li NMR studies yield kinetic and
equilibrium data as exemplified by $k_f = 6.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
and $k_d = 107 \text{ s}^{-1}$ at 298.2 K in dimethylformamide
for the equilibrium:-



The structural, kinetic and equilibrium aspects of
[Li.C21C₅]⁺ are discussed in conjunction with data from
related systems.

SOLVENT EXCHANGE ON HEXAKIS(METHANOL)COPPER(II) ION. A
 ^{17}O NMR VARIABLE TEMPERATURE, PRESSURE, AND FREQUENCY
 STUDY.

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 Donald Zbinden^A.

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 University of Adelaide, Adelaide, South Australia 5001

The high lability of $[\text{Cu}(\text{solvent})_6]^{2+}$ towards ligand
 substitution has been attributed to the tetragonal
 distortion of six-coordinate copper(II), and at the same
 time has made mechanistic studies difficult. This ^{17}O FT
 NMR variable pressure, temperature, and frequency study
 of methanol exchange on $[\text{Cu}(\text{MeOH})_6]^{2+}$ yields: $k(298.2\text{ K})$
 $= (3.09 \pm 0.46) \times 10^7\text{ s}^{-1}$, $\Delta H^\ddagger = 17.16 \pm 0.81\text{ kJ mol}^{-1}$,
 $\Delta S^\ddagger = -43.96 \pm 3.95\text{ J K}^{-1}\text{ mol}^{-1}$, and $\Delta V^\ddagger = 8.34 \pm 0.35$
 $\text{cm}^3\text{ mol}^{-1}$ (the first ΔV^\ddagger reported for $[\text{Cu}(\text{solvent})_6]^{2+}$).
 The mechanistic implications of these data are discussed
 in conjunction with those for the analogous Mn^{2+} , Fe^{2+} ,
 Co^{2+} , and Ni^{2+} systems.

SIX-COORDINATE TRIVALENT LANTHANIDES AND UNUSUALLY SLOW
MONODENTATE LIGAND EXCHANGE PROCESSES.

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The trivalent lanthanide $[\text{Ln}(\text{solvent})_n]^{3+}$ species are characterised by $n = 9$ for water, $n = 8$ for dimethylformamide (dmf), and $n = 6$ for 1,1,3,3-tetramethylurea (tmu). This decrease in coordination number is accompanied by a marked decrease in coordinated solvent lability. Thus for exchange of tmu on $[\text{Tm}(\text{tmu})_6]^{3+}$ $k(298.2 \text{ K}) = 145 \text{ s}^{-1}$, $\Delta H^\ddagger = 29.3 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -105 \text{ J K}^{-1} \text{ mol}^{-1}$, and similarly slow tmu exchange is observed on other $[\text{Ln}(\text{tmu})_6]^{3+}$ species. In contrast $[\text{Tm}(\text{dmf})_8]^{3+}$ is characterised⁽¹⁾ by $k(298.2 \text{ K}) = 3.1 \times 10^7 \text{ s}^{-1}$, $\Delta H^\ddagger = 33.2 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 9.9 \text{ J K}^{-1} \text{ mol}^{-1}$, and $[\text{Ln}(\text{OH}_2)_9]^{3+}$ species are characterised by $k(298.2 \text{ K}) = 10^8 - 10^9 \text{ s}^{-1}$. The origins of these changes in coordination number and lability, and the mechanistic implications will be discussed.

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THE EFFECT OF SOLVENT SIZE ON LABILITY. A NUCLEAR MAGNETIC
 RESONANCE STUDY OF SOLVENT EXCHANGE ON HEXAKIS(N,N-DI-
 METHYLACETAMIDE)COBALT(II), HEXAKIS(N,N-DIETHYLFORM-
 AMIDE)COBALT(II), AND THEIR NICKEL(II) ANALOGUES.

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 Boffa.

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^1H NMR studies of N,N-diethylformamide (def) exchange
 on $[\text{Co}(\text{def})_6]^{2+}$ and $[\text{Ni}(\text{def})_6]^{2+}$ yield $10^{-3} k(298.2 \text{ K}) =$
 (120 ± 16) and $(1.15 \pm 0.08) \text{ s}^{-1}$; $\Delta H^\ddagger = 51.4 \pm 2.0$ and
 $74.2 \pm 1.1 \text{ kJ mol}^{-1}$; and $\Delta S^\ddagger = 24.8 \pm 7.0$ and $62.6 \pm 3.4 \text{ J K}^{-1}$
 mol^{-1} respectively. ^{13}C NMR studies of N,N-dimethyl-
 acetamide (dma) exchange on $[\text{Co}(\text{dma})_6]^{2+}$ and $[\text{Ni}(\text{dma})_6]^{2+}$
 yield $10^{-6} k(298.2 \text{ K}) = (23.1 \pm 3.5)$ and $(3.52 \pm 0.70) \text{ s}^{-1}$;
 $\Delta H^\ddagger = 32.7 \pm 0.8$ and $40.4 \pm 1.8 \text{ kJ mol}^{-1}$; and $\Delta S^\ddagger =$
 5.8 ± 3.0 and $16.0 \pm 10.0 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. These
 systems are also characterised by equilibria between
 tetrakis- and hexakis(solvent) species, and the latter
 species are considered to undergo exchange through D
 mechanisms. The greater lability of the dma species is
 attributed to the increased steric crowding caused by the
 acetyl moiety. These results are discussed in conjunction
 with reported studies of related systems.

REACTIONS OF TUNGSTEN OXIDE TETRAFLUORIDE
IN ANHYDROUS HYDROGEN FLUORIDE

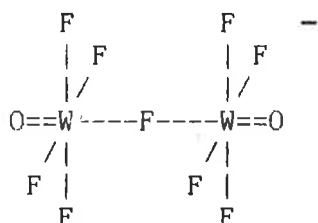
Bernard F. Hoskins, Anthony Linden, and Thomas A. O'Donnell

Department of Inorganic Chemistry, University of Melbourne,
Parkville, Victoria, 3052, Australia.

Tungsten oxide tetrafluoride acts as a weak Lewis acid in anhydrous hydrogen fluoride (AHF). A number of reactions between WOF_4 and fluoride donors have been studied, using donors such as ClF_3 , XeF_2 and NO_2F . Raman spectroscopy has shown that when WOF_4 acts as a Lewis acid in AHF, the anion generated is invariably the fluorine bridged dimeric $\text{W}_2\text{O}_2\text{F}_9^-$ rather than WOF_5^- . The W=O vibrational stretching frequency can be used as a diagnostic to determine the nature of the tungsten oxide fluoride species present. Reactive fluoride donors tend to abstract oxygen from WOF_4 . With XeF_2 reaction (a) was found to occur.



The crystalline adducts $[\text{NO}_2^+][\text{W}_2\text{O}_2\text{F}_9^-]$, 1, $[\text{ClO}_2^+][\text{W}_2\text{O}_2\text{F}_9^-]$, 2, and $[\text{H}_3\text{O}^+][\text{W}_2\text{O}_2\text{F}_9^-]$, 3, have been prepared and their crystal structures determined. The arrangement of the atoms within the anion is shown below. The structures are all very similar, except that the anion in 3 has a bent fluorine bridge, while 1 and 2 have linear anions. This can be explained on the basis of the close packing of the fluorine atoms. Cubic close packing yields a linearly bridged anion, while hexagonal close packing results in a bent bridge. The structures are predominantly ionic with virtually no covalent interaction between the cation and anion. This reflects the high fluoride donor ability of the Lewis base system, rather than providing an indication of the Lewis acid strength of WOF_4 .

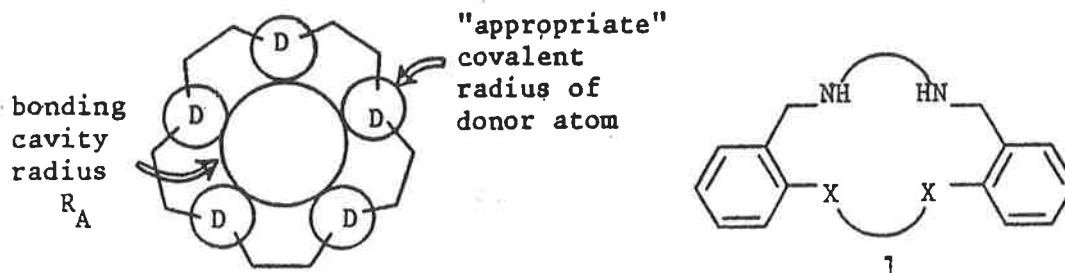


SPECIFICATION OF BONDING CAVITIES AVAILABLE IN METAL-BINDING SITES: A COMPARITIVE STUDY OF MACROCYCLIC NICKEL COMPLEXES

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A procedure has been developed for specifying the bonding cavities presented by multidentate ligands. X-ray data are used to obtain the mean distance of the donor atoms from their centroid. The resulting radius of the "hole" (R_H) defined by the nuclear positions of the donor atoms is corrected to allow for the covalent radii of the donor set to yield the radius (R_A) of the "bonding cavity" available to the metal ion. For coordinated macrocycles the ratio of the bonding cavity radius (R_A) to the Pauling covalent radius provides a measure of the goodness-of-fit of the macrocycle's donor set for the metal ion. Calculations of this type have been very successful⁽¹⁾ in matching hole-size data with the properties of high-spin Ni(II) complexes of the general type 1.



The procedure can be applied to metal-free macrocycles and can be used to obtain a direct comparison of the relative hole-sizes in coordinated and uncoordinated states. It can also be applied to systems which incorporate uneven numbers of donor atoms and/or irregular coordination geometries - no other simple procedure is available to do this.

Bonding cavity radii have been calculated for 110 macrocyclic Ni(II) complexes and related free ligands for which X-ray data are available. This survey has allowed us to establish certain "rules-of-thumb" which predict how cavity hole size will vary with changes in structural features of the macrocyclic ligands. Such "rules-of-thumb" will be applied to ligand design in attempts to develop more highly selective complexing agents for transition- and base-metal ions.

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Crystal Structures of $\text{SiCo}_4(\text{CO})_{14}$, $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ and $\text{GeFe}_2\text{Co}_4(\text{CO})_{22}^-$: Some Relationships with $\text{GeCo}_4(\text{CO})_{14}$.

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School of Science, University of Waikato, Hamilton, New Zealand.

Spectroscopic evidence indicated that a number of species have open chain structures of linked GeCo_2 triangles, as established crystallographically for $\text{GeCo}_4(\text{CO})_{14}$ (I), but single crystals have remained elusive. Recently, the silicon analogue, $\text{SiCo}_4(\text{CO})_{14}$ (II) and the homologue $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (III) have been solved and will be reported.

(I) is known to react with $\text{Mn}(\text{CO})_5^-$ or $\text{Co}(\text{CO})_4^-$ to form different mixed metal clusters, and has now been shown to form $\text{GeFe}_2\text{Co}_4(\text{CO})_{22}^-$ (IV) with $\text{Fe}_2(\text{CO})_8^{2-}$. The structure of (IV) will be presented. In contrast, (II) reacts with any of the metal carbonyl anions to form the same species, $\text{SiCo}_9(\text{CO})_{21}^{2-}$ (V), which has been reported. Further studies on (V) will be discussed.

Characterisation of Tris(diselenocarbamato)cobalt(III) and Pentakis(diselenocarbamato)dichlorocobalt(III) Complexes by Electrochemical, Cobalt-59 N.M.R. and Mass Spectrometric Techniques - Comparisons with Dithiocarbamate Analogues.

A.M. Bond¹, R. Colton², D.R. Mann¹

Contribution from: (1) The Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds, Victoria 3217 and (2) The Division of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, 3052.

A series of $\text{Co}(\text{RR}'\text{dsc})_3$ and $[\text{Co}_2(\text{RR}'\text{dsc})_5]^+$ complexes ($\text{R}, \text{R}' =$ two alkyl groups or one heterocyclic group; $\text{dsc} = \text{NCSe}_2$) have been synthesised and their redox behaviour, chemical reactivity and spectroscopic properties compared with the corresponding dithiocarbamate ($\text{RR}'\text{dte}$) complexes.

Electrochemical oxidation of $\text{Co}(\text{RR}'\text{dsc})_3$ in dichloromethane at platinum electrodes occurs at potentials about 0.34 V less positive than for $\text{Co}(\text{RR}'\text{dte})_3$. The formally cobalt(IV) complexes $[\text{Co}(\text{RR}'\text{dsc})_3]^+$ can be identified as a product which is then converted to $[\text{Co}_2(\text{RR}'\text{dsc})_5]^+$ via dimerization and an internal redox reaction. $\text{Co}(\text{RR}'\text{dsc})_3$ is reduced at fairly negative potentials on both platinum and mercury electrodes with extremely rapid loss of $[\text{RR}'\text{dsc}]^-$. The $[\text{Co}_2(\text{RR}'\text{dsc})_5]^+$ complexes are also more readily oxidised and harder to reduce than the sulphur analogues. Oxidation of $[\text{Co}_2(\text{RR}'\text{dsc})_5]^+$ produces $[\text{Co}_2(\text{RR}'\text{dsc})_5]^{2+}$ at low temperatures and fast scan rates, but no stable reduced form of the dimer is accessible on the voltammetric time scale examined. The reduction process for the dimer is consistent with the reaction $[\text{Co}_2(\text{RR}'\text{dsc})_5]^+ + e^- \rightarrow \text{Co}(\text{RR}'\text{dsc})_3 + \text{Co}(\text{RR}'\text{dsc})_2$. Electrochemical oxidation data obtained at mercury electrodes for the diselenocarbamate complexes are complicated by adsorption but are similar to that found at platinum electrodes. This contrasts with the dithiocarbamates where a mercury electrode specific pathway is observed.

Cobalt-59 n.m.r. spectroscopy in dichloromethane shows the non-equivalence of the two cobalt atoms in $[\text{Co}_2(\text{RR}'\text{dsc})_5]^+$. The chemical shifts for $\text{Co}(\text{RR}'\text{dsc})_3$ complexes exhibit similar substituent effects to the dithiocarbamates in cobalt-59 n.m.r. measurements as was the case in oxidative electrochemistry. Cobalt-59 n.m.r. spectroscopy and mass spectrometry demonstrate that exchange, substitution and redox reactions can lead to the formation of mixed ligand diselenocarbamate complexes and mixed dithiocarbamate/diselenocarbamate complexes for both the cobalt(III) monomers and dimers.

Ab Initio Calculations on Sulphur Compounds I;
 Thiocarbonates, the Force Field of Methyl Xanthate, and the Shape of
 $\text{XC}\equiv\text{SF}_3$ ($\text{X} = \text{H}, \text{F}, \text{CH}_3$).

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We have undertaken a systematic theoretical study of the series $\text{CO}_n\text{S}_{3-n}^{2-}$, and their protonated and methylated derivatives. Little experimental information is available for most of these systems. Bond lengths, bond angles, bond stretching force constants and overlap populations are presented. Most of the structural variation in this series can be interpreted in terms of π bonding, which is less efficient between C and S than between C and O.

The complete force field of the methyl xanthate anion has been calculated. The average error in predicted frequencies is about 2%. There is very extensive mixing of the C-O stretch, the O-C stretch, the C-S₂ stretches, and several bending modes.

The first compound containing a formal C \equiv S triple bond has recently been prepared by K. Seppelt and co-workers. Most surprisingly the C-C \equiv S skeleton in $\text{CF}_3\text{C}\equiv\text{SF}_3$ is non-linear at the central C. We have calculated the bending potentials for three different $\text{XC}\equiv\text{SF}_3$ derivatives ($\text{X} = \text{H}, \text{F}, \text{CH}_3$). All are predicted bent at the central carbon, once the effects of electron correlation are included, but by substantially differing amounts. We predict that $\text{XC}\equiv\text{PH}_2$ species will also be non-linear at C.

"SPIN EQUILIBRIUM IN FERROUS CAGE COMPLEXES"

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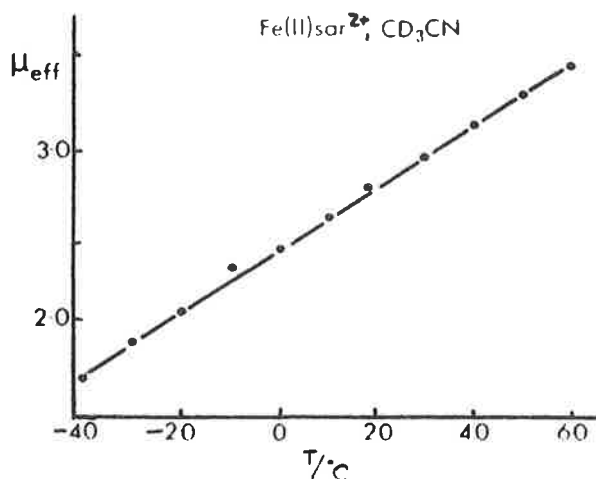
Encapsulation of the ferrous ion by the ligands sar, [1]; $(\text{NH}_2)_2\text{sar}$, [2]; and $(\text{NH}_3)_2\text{sar}$, [3]; has resulted in a series of complexes which exhibit spin equilibria in solution.

This spin condition has been studied using variable temperature electronic spectroscopy and ^1H NMR spectroscopy. The position of the equilibrium can be ascertained using the contact shifted resonances with good accuracy.

Analysis of the absorption spectrum is centred about the low spin bands, which are usually an order of magnitude more intense than the high spin transitions.

The energy separation between the ^1A and $^5\text{T}_2$ levels has been estimated based upon a simple model with the ^1A lying lowest. Other parameters of thermodynamic significance have also been evaluated.

The solution magnetic behaviour is in direct contrast to that found in the solid state for complexes [1] and [3]. In these cases the high spin condition is maintained from 300 K down to 4.2 K. It is anticipated that [2], will show somewhat different spin characteristics in the solid state and this is currently under investigation.



R = H [1]
R = NH_2 [2]
R = NH_3 [3]

REACTIONS OF BIS(DIPHENYLPHOSPHINO)ACETYLENE WITH VARIOUS CLUSTERS AND SUBSEQUENT REACTIVITY OF AN OPEN Ru₅ CLUSTER WITH SMALL MOLECULES

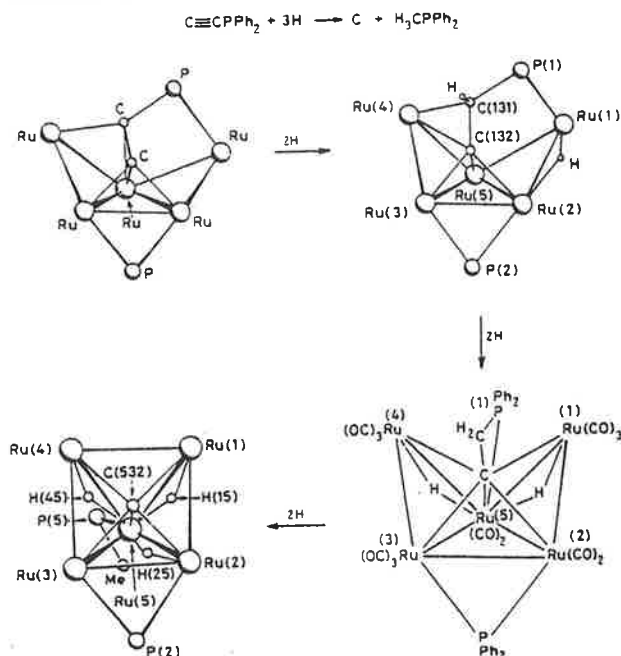
M.I. Bruce, J.G. Matisons and M.L. Williams

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001.

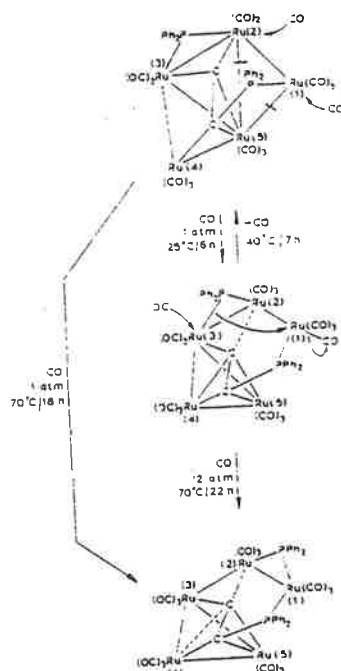
Recently it was shown that specific carbonyl substitution of various clusters could be achieved by electron-transfer-catalysed (ETC) reactions with phosphine donor ligands. The application of this reaction to the sequential incorporation of various ligands allows designed syntheses of Ru₃(CO)₁₂ derivatives. Sodium diphenylketyl is the preferred ETC catalyst. The utility of these syntheses has allowed the chemistry of novel, functionally-substituted phosphines coordinated to Ru₃ clusters to be investigated.

Bis(diphenylphosphino)acetylene (dppa) reacts readily under mild conditions with Ru₃(CO)₁₂ to form [Ru₃(CO)₁₁]₂(μ-dppa) in high yield. Subsequent thermal rearrangement of this complex results in the formation of black Ru₅(μ₅-η²-C₂PPh₂)(μ-PPh₂)(CO)₁₃ in good yield. The reactivity of the latter complex was investigated with a variety of reagents. For instance, hydrogenation proceeds stepwise with the absorption of three molecules of H₂ and successive formation of penta-nuclear cluster complexes containing μ₅-vinylidene, μ₄-methylidyne, and μ₅-carbide ligands (see Scheme 1). These unusual reactions eventually result in a novel reduction of the acetylide ligand to carbon and methyl.

Scheme 1



Scheme 2



The complex, Ru₅(μ₅-C₂PPh₂)(μ-PPh₂)(CO)₁₃ also reacts with CO to form a variety of products. The reaction is very sensitive to slight variations in either temperature or CO pressure (Scheme 2). Structural studies will be presented on several unusual products isolated from these reactions.

EFFECT OF SODIUM ION INTERFERENCE ON BIOINORGANIC FORMATION CONSTANTS DETERMINED BY GLASS ELECTRODE POTENTIOMETRY

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Recently, a library of computer programs for the determination of metal-ligand formation constants, called ESTA (Equilibrium Simulation for Titration Analysis), has been developed [1]. These programs permit various corrections which are important in the measurement of thermodynamic parameters required by those modelling metal-ion interactions in biological fluids [2]. Changes in ionic activities, liquid junction potentials and ion-selectivity of the electrodes can be calculated [3].

The formation constants of many formation constants of bioinorganic importance are such that pH measurements need to be made in relatively alkaline solutions where sodium ion interference with the glass electrode response is most pronounced. The object of the present work was to quantify the effect of such interference and to assess the seriousness of neglecting it in a typical study of a metal-ligand interaction with bioinorganic interest.

Potential differences arising from the presence of sodium ions in the titration solutions were characterised in terms of two parameters, K and α . K is the selectivity coefficient in the Nickolsky equation [4] when $\alpha = 1$. Data were collected experimentally and from the literature [5,6]. Titration data for the binding between Zn(II) and the amino acid, cysteine [6,7] were then analysed using the ESTA program.

The results show that significant systematic errors have affected many bioinorganic formation constants determined in sodium ion background electrolyte solutions. However, with modern glass electrodes the magnitude of these errors is probably about the same as those arising from other sources (such as errors in the analytical concentrations). Nevertheless, they are sufficiently large to warrant attention in future determinations of formation constants for bioinorganic purposes.

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3. P. M. May, K. Murray and D. R. Williams, Talanta, 1985, 32, 483.
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REDOX AND LIGAND SUBSTITUTION CHEMISTRY OF TRIAMMINETRIAQUO-RUTHENIUM(III).

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As its triflate salt, the title complex, $\text{Ru}(\text{NH}_3)_3(\text{OH}_2)_3^{3+}$ (A), is a useful starting material for a large range of redox and ligand substitution reactions. Using electrochemical methods (CV, Differential Pulse and Square Wave Methods), the reduction of (A) to $\text{Ru}(\text{NH}_3)_3(\text{OH}_2)_3^{2+}$ (B) and its oxidation to the Ruthenyl complex, $\text{Ru}(\text{NH}_3)_3(\text{OH}_2)_2(\text{O})^{2+}$ (C), have been studied.

Ligand substitution of the coordinated water molecules on both (A) and (B) occurs quite readily. The rate of substitution on (A) is enhanced by a partial (and reversible) reduction of (A) to (B). Such ligand substitutions have involved polypyridines, organonitriles, diketonates, carboxylates and halides. Solvolysis of the coordinated water molecules by organic solvents was also studied by electrochemical techniques.

Radiation Induced Dissolution of Colloidal Manganese Oxides

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ABSTRACT

The crystal structure of metal oxides is known to play an important role in the reactivity of the oxide to various redox processes in solution. Studies of the role of the crystal structure have, however, been complicated by the effects of reactant adsorption, surface area, hydration, lattice impurities or because of inadequate control of solution conditions.

Manganese dioxide is one such metal oxide. Its structure is crucial in determining its efficiency in dry cell batteries, as a selective oxidant in organic chemistry or as an adsorbent of polluting agents such as SO_2 or heavy metals such as Pb.

In this study, ionising radiation has been used to generate radicals in solution which can dissolve colloidal suspensions of various manganese oxides. It has been shown that the reaction occurring can be written as:



The dissolution process can be followed by the production of $\text{Mn}^{2+}(\text{aq})$. Several manganese oxides have been studied with a view to establishing the effect of the crystal structure upon the surface redox reaction leading to dissolution.

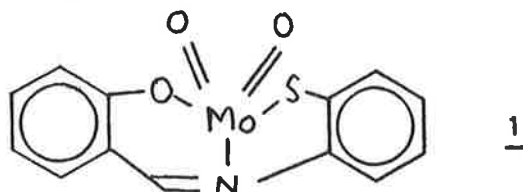
REACTIONS OF OXOMOLYBDENUM(VI) S-DONOR CHELATES WITH ORGANOHYDRAZINES

G.D. Fallon,^(a) M.D. FitzRoy,^(a) J.M. Frederiksen,^(b)K.S. Murray,^(a) M.R. Snow^(b) and E.R.T. Tiekink^(b)

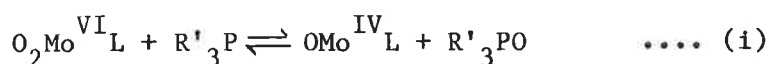
a) Department of Chemistry, Monash University

b) Department of Chemistry, University of Adelaide

As a continuation of the work presented at COMO 12¹ we have studied the reactions of the cis-dioxomolybdenum(VI) moiety with organohydrazines, not only as a function of donor atom variations (O vs. S) within the co-ligand but also as a function of overall coordination number (five vs. six coordinate). Structural variations are described for the multiply bonded MoO_2^{2+} , $\text{Mo}(\text{O})(\text{N}_2\text{Ph}_2)^{2+}$ and $\text{Mo}(\text{N}_2\text{Ph})_2^{2+}$ fragments in six-coordinate thiohydroxamate complexes of type $\text{Mo}(\text{X})(\text{Y})(\text{PhCS.NMeO})_2$. Comparisons are made with related systems possessing other S-donor co-ligands.² To see if coordination number around Mo influences these kinds of condensation reactions we have monitored the structure of the MoO_2^{2+} moiety in the Schiff base complex, 1, before and after its reaction with R_2NNH_2 .



Interestingly, and perhaps surprisingly, the complex 1 is capable of undergoing the biologically related O-atom transfer reaction (i),



without formation of the oxo-bridged Mo^{V} dimer, $(\text{OMoL})_2$.³ The apparent structural simplicity of 1 contrasts with the impressively designed five-coordinate species of Berg and Holm, recently also shown to undergo reaction (i).⁴

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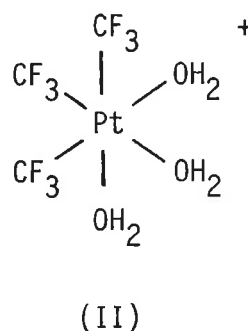
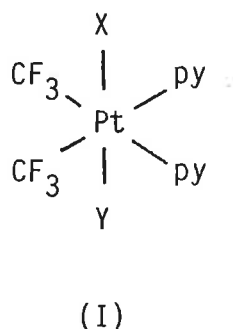
TRIFLUOROMETHYL-PLATINUM COMPOUNDS

Trevor G. Appleton, John R. Hall and Don. W. Neale

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Norbornadiene, NBD, is readily displaced from $\text{Pt}(\text{CF}_3)_2(\text{NBD})$ by a range of ligands, including pyridine (py), NH_3 , ethylenediamine, RCN, dmsO, dmf, acac^- , I^- . Many of these complexes are readily hydrolysed by traces of water, giving initially HF and coordinated CO.

Cis- $\text{Pt}(\text{CF}_3)_2\text{py}_2$ reacts with reagents XY by oxidative addition to give $\text{Pt}(\text{CF}_3)_2\text{XYpy}_2$ (I) ($\text{XY} = \text{Cl}_2, \text{Br}_2, \text{I}_2, \text{MeI}, \text{CF}_3\text{I}$). $\text{Pt}(\text{CF}_3)_3\text{Ipy}_2$ with aqueous acid and silver ion gives fac- $\text{Pt}(\text{CF}_3)_3(\text{H}_2\text{O})_3^+$ (II). The chemistry of tris-(trifluoromethyl) platinum(IV) compounds differs markedly from that of the well-known trimethylplatinum(IV) complexes. For example, (II) with halide ions, X^- , gives complexes $\text{Pt}(\text{CF}_3)_3\text{X}_n(\text{H}_2\text{O})_{(3-n)}^{(n-1)-}$. No analogues of $[\text{PtMe}_3(\mu_3\text{-X})]_4$ are formed.



**REDOX REACTIONS OF BIS(DIETHYLDITHIOCARBAMATO)Mo^{VI} OXO AND
IMIDO COMPLEXES WITH Fe^{II} and Mn^{II}**

Robyn L. Elliott, Peter J. Nichols and Bruce O. West

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Homobinuclear Mo^V dithiocarbamate complexes can be formed by redox reactions between Mo^{VI}O₂ and Mo^{IV}O complexes.¹ Thus



Similar reactions between the diethyldithiocarbamate complex (Et₂dtc)₂Mo^{VI}O₂ and Fe^{II} and Mn^{II} complexes of salicylideneimines and dithiocarbamates have been found to lead to heterobinuclear oxo bridged complexes (dtc)₂Mo^V(O)OFe(Mn)^{III}(Lig). The Mo-O-Fe derivatives show evidence for magnetic coupling at room temperature, e.g. μ_{eff} for (Et₂dtc)₂Mo(O)OFe(salen) is 5.3 B.M. at 300K compared to the uncoupled spin only value per molecule for a d¹-d⁵ system of 6.2 B.M. Mo-O-Mn complexes, e.g. (Et₂dtc)₂Mo(O)OMn(Et₂dtc)₂ has μ_{eff} = 5.2 B.M. which is essentially the spin only value for a d¹-d⁴ uncoupled system. The organoamido group:NR being isoelectronic with the oxo group may be considered also likely to form imido bridged derivatives.

The diimido complex (Et₂dtc)₂Mo^{VI}(NPh)₂ and the mixed derivative (Et₂dtc)₂Mo^{VI}(O)(NPh) have been reported previously² and the latter has been reacted with (Et₂dtc)₂Mo^{IV}(NPh)₃ although the product is considered to be an oxo bridged derivative, [(Et₂dtc)₂Mo(NPh)]₂O.

These two imido complexes have also been found to react with Fe(salen). (Et₂dtc)₂Mo(O)(NPh) gives rise to a product which no longer displays an Mo=O stretching frequency and, therefore, is considered to be an oxo bridged derivative (Et₂dtc)₂Mo(NPh)OFe(salen). The diimide derivative forms a mixture of products, one of which contains both Mo and Fe according to electron microprobe analysis and in general properties appears to be the first bridged imido heterobinuclear species to have been recognised. Its tentative formula is (Et₂dtc)₂Mo(NPh)-N(Ph)-Fe(salen).

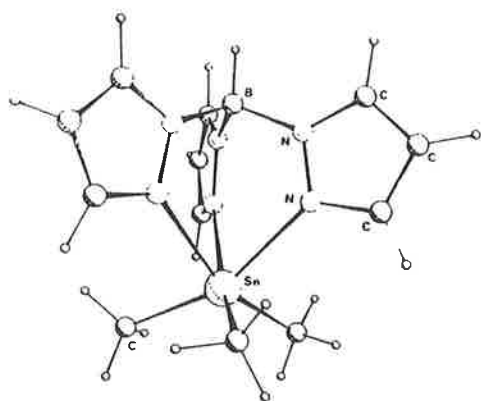
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2. Maata, E.A. and Wentworth, R.A.D., *Inorg. Chem.*, **18**, 2404 (1979).
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Poly(pyrazolyl)borate Complexes of the Methyl Tin Chlorides.

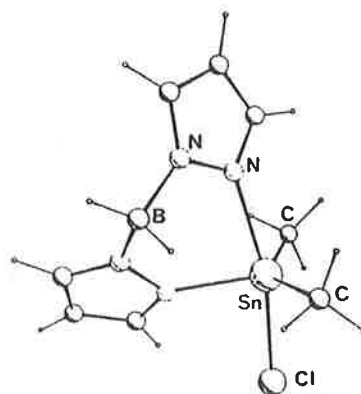
Brian K. Nicholson, Siew Kim Lee and Owen J. Curnow.

School of Science, University of Waikato, Hamilton, New Zealand.

The reaction of $K[(pz)_3BH]$ ($pz = 1\text{-pyrazolyl} = C_3N_2H_3$) with Me_xSnCl_{4-x} ($x = 0 - 3$) gives the six-coordinate complexes $Me_xSnCl_{3-x}[(pz)_3BH]$ ($x = 0 - 3$). Similarly the five-coordinate $Me_xSnCl_{3-x}[(pz)_2BH_2]$ can be prepared using $K[(pz)_2BH_2]$. The structures of $Me_3Sn[(pz)_3BH]^1$, (1) and of $Me_2ClSn[(pz)_2BH_2]$, (2), confirm the coordination of all the pz rings of each pyrazolyl-borate ligand in the solid state and ^{119}Sn n.m.r. spectra indicate the structures of (1) and (2) are maintained in solution.



(1)



(2)

Reactions of $Cl_3Sn[(pz)_3BH]$ with $Co(CO)_4^-$ are complicated; products include the anions $[Co(CO)_3\{SnCl_2[Co(CO)_4]\}_2]^-$ and $[Co(CO)_3\{SnCl[Co(CO)_4]\}_2]^-$ isolated as their $[Co\{(pz)_3BH\}_2]^+$ salts² and characterised by X-ray crystallography.

(1) B.K. Nicholson, *J. Organometal. Chem.*, **265**, (1984), 153.

(2) O.J. Curnow & B.K. Nicholson, *J. Organometal. Chem.*, **267**, (1984), 257.

DYNAMICS OF BERYLLOCENE INVERSION BY ^{13}C NMRKerry W. Nugent and James K. Beattie

School of Chemistry, University of Sydney

The observation of partially relaxed coupling to ^9Be in the ^{13}C nmr spectrum of beryllocene in solution leads to an estimate of 10^{10} s^{-1} for the rate of molecular inversion.

Crystalline beryllocene is a 'slip-sandwich', with the beryllium centrally bonded to one of the Cp rings and peripherally bonded to the other. In solution the low-temperature ^1H nmr spectrum comprises a single resonance, indicating that the protons of both Cp rings are magnetically equivalent.

The ^1H decoupled ^{13}C spectrum also displays a single resonance but with fine structure that arises from coupling between ^{13}C and the partially relaxed quadrupolar beryllium nucleus (100% ^9Be , $I = 3/2$). As the solution temperature is decreased the ^{13}C linewidth decreases, i.e. the relaxation of the beryllium nucleus becomes more rapid, and the lineshape approaches a sharp singlet at around 200 K in diethyl ether solution. The lineshape is virtually the same in both cyclohexane and diethyl ether solutions, despite the fact that these two solvents have significantly different viscosities. If the relaxation of the quadrupolar ^9Be were due to tumbling of the polar molecule in solution, the relaxation correlation time would depend on solvent viscosity. In this case the relaxation time of the ^9Be nucleus would be significantly shorter in the cyclohexane solution than in the ether solution. This is not observed. These observations imply that the relaxation process is not due to molecular reorientation and the correlation time is consequently longer than the 10^{-11} s tumbling time. A consistent interpretation of these results is that the quadrupolar nucleus is relaxed by inversion of the molecular dipole caused by exchange of the beryllium between the two Cp rings, a process which occurs with a correlation time of the order of 10^{-10} s .

Stabilization of Unusual Cationic Species in Highly Acidic Media

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University of Melbourne,
Parkville, Victoria 3052. Australia.

The Gillespie group has done much to characterize homopolyatomic cations of non-metals in superacidic media such as oleums and HSO_3F ; and they have crystallized many of these cations under non-basic conditions and determined their structures. Some typical examples are I_2^+ , I_3^+ , Br_3^+ , Cl_3^+ , S_4^{2+} , S_8^{2+} , Se_{10}^{2+} and Te_6^{4+} .

At Melbourne we have used controlled amounts of F_2 in HF to generate I_2^+ and I_3^+ in solution and have demonstrated a marked dependence of cation speciation on the extent of basicity of the solution. We have shown this dependence to be general for all protonic superacids. Non-metal cations undergo stepwise disproportionation by interaction with the base of the system. A typical overall disproportionation would be:



where X^- represents the bases HSO_4^- , SO_3F^- or F^- of the superacid solvent systems H_2SO_4 , HSO_3F or HF. In exactly analogous fashion, stable I_2^+ can be formed in the acidic melt AlCl_3 but disproportionates to I_2 and ICl as the base Cl^- is added.

The Melbourne group has exploited the reversibility of the disproportionation reactions by producing I_2^+ from reaction of I_2 and IF_5 in HF made acidic with SbF_5 . Similarly control of the stoichiometry of reaction between S_8 and SF_4 in acidic HF has led to formation of either S_8^{2+} or S_4^{2+} . More recently we have been reacting P_4 and PF_3 in HF/ SbF_5 to produce polyatomic cations of phosphorus.

Since 1976 we have been producing stable solutions in acidic HF of transition metal cations in very low oxidation states which would be unstable in basic solvents such as water, e.g. V^{2+} , Ti^{2+} , Zr^{3+} , U^{3+} , Sm^{2+} etc. We have characterized these cations by solution spectroscopy. Most recently we have shown that base-induced disproportionation occurs for some of these monatomic cations also. Addition of F^- to a stable lilac-coloured solution of U^{3+} gave a green precipitate of UF_4 and a mirror of metallic uranium.

AXIAL LIGATION IN A COBALT BIS-POCKET PORPHYRAZINE**S.W. Oliver****Chemistry Department, Monash University, Clayton, Victoria, 3168.**

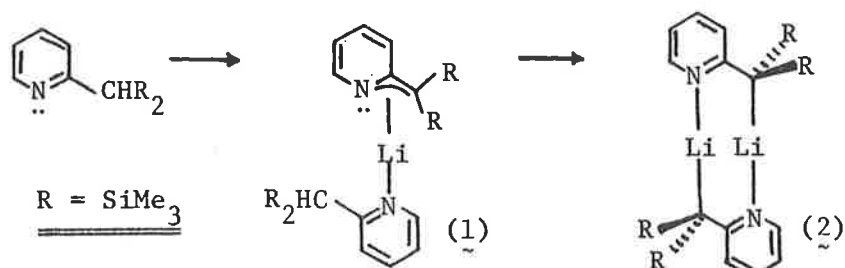
A bis-pocket porphyrazine has been used to duplicate the strong ligand field found in phthalocyanines. The benzene-soluble cobalt chelate has enabled the effect of varying axial ligation, ranging from a freedom of axial ligation to bis-pyridine, tetrahydrofuran, thiophen, N-methyl imidazole and water adducts, to be studied by e.s.r. spectroscopy. E.s.r. parameters have been obtained in each case and correlated with base properties.

Functionalized Alkyl-Lithium Chemistry

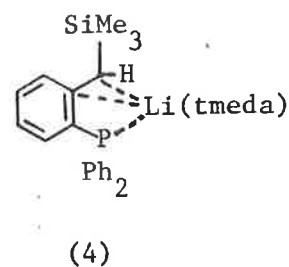
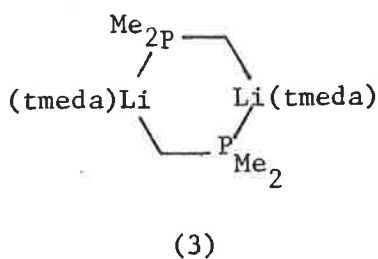
Rocco I. Papasergio, Colin L. Raston, and Allan H. White.

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A., 6009.

The presence of a functional group in organic compounds, RH, can greatly affect the nature of the lithiation product obtained, as can steric effects of RH and the choice of reaction solvent. In a systematic study on the metallation of $2-(\text{Me}_3\text{Si})_{3-n}\text{CH}_n\text{C}_5\text{H}_4\text{N}$, using nBuLi in a variety of solvents and with different degrees of substitution, $n = 1, 2$ or 3^1 , a diverse range of products have been obtained. In hexane with $n = 1$, for example, compound (1) is obtained, contrasting with no metallation under the same conditions for the isoelectronic compound $(\text{Me}_3\text{Si})_2\text{CHC}_6\text{H}_5$. Another example is that compound (1) further reacts with n-BuLi only in the presence of a Lewis base yielding, in the case of OEt_2 , the 'ether free' complex (2). (1) has a novel n^3 -aza-allyl ligand to metal interaction.



Metallation of phosphorus functionalized alkyls has also been investigated. Results to date include the formation of (3) & (4) respectively from PMe_3 and $\text{O}-\text{PPh}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_3$.



* tmeda = N,N,N',N'-tetramethylethylenediamine

1. R.I. Papasergio, C.L. Raston and A.H. White, J. Chem. Soc., Chem. Commun. 1984, 1708.
2. L.M. Engelhardt, G.E. Jacobsen, C.L. Raston and A.H. White, J. Chem. Soc. Chem. Commun., 1984, 220

**SOLUTION BEHAVIOUR AND OXIDATION OF ISOCYANIDE
DIRHODIUM COMPLEXES**

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Co-ordinative addition of a variety of ligands L to the mono-carbonyl complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ gives stable adducts of the type $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})\text{L}(\text{CF}_3\text{C}_2\text{CF}_3)$ (e.g. L = CO, *t*-BuNC, PPh₃).¹ A similar reaction occurs with 2,6-Me₂C₆H₃NC, but the corresponding reactions with other isocyanides, RNC (R = Et, *i*-Pr, Cy, *p*-MeOC₆H₄, *p*-NO₂C₆H₄, Ph) proceed in a different manner. There is isomerization of the initial reaction product, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CNR})(\text{CF}_3\text{C}_2\text{CF}_3)$, A, to a more stable species, B, in solution. The rate of conversion of A to B depends on R and ranges from $t_{1/2} = 15$ hrs. when R = *i*-Pr to $t_{1/2} = <1$ min. in the case of R = *p*-NO₂C₆H₄. Variable temperature ¹H and ¹⁹F NMR experiments indicate B exists as at least three isomers in solution; however, only one of the isomers can be isolated in the solid state. The crystal structure of B (R = Et) has been determined, and indicates an acyl bridging isocyanide and a terminal carbonyl.

Treatment of these isocyanide adducts with trimethylamine-N-oxide under refluxing conditions in acetone results in formation of the complex, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\mu_2\text{-}\eta^3\text{-CF}_3\text{C}_2\text{CF}_3\cdot\text{C}(\text{O})\text{NR}\}$, C. The bound isocyanide is oxidized to an isocyanate, which condenses with the alkyne to form a bridging acrylamide ligand. These compounds, C, have previously been isolated via two other synthetic routes.²

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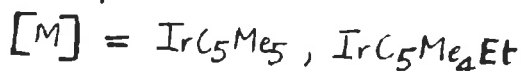
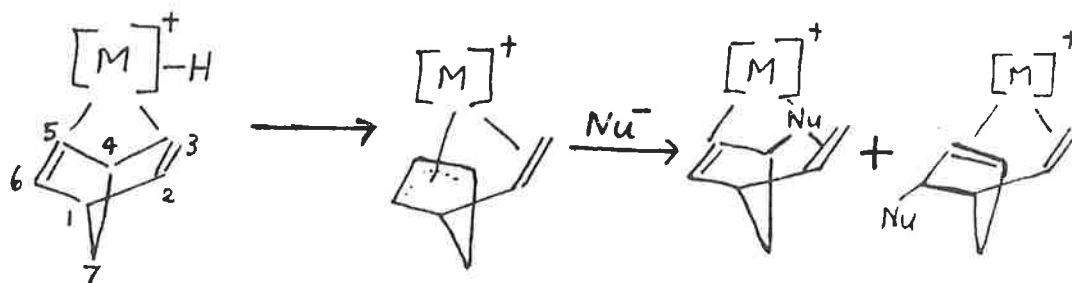
PROTONATION REACTIONS OF NORBORNADIENE COMPLEXES OF RHODIUM AND IRIUM

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GPO Box 4, Canberra, ACT 2601.

The protonation of the complexes $M(\eta^5-C_5R_5)(nbd)$ ($M = Rh, R = H, Me; M = Ir, R = Me, Et; nbd = norbornadiene$) has been studied as part of a program concerned with the action of acids on metal diene complexes. Lewis *et al.*¹ claimed that the species present in CF_3COOH solutions of $Rh(\eta^5-C_5H_5)(nbd)$ was the 16e norbornenylrhodium(III) cation. We find that, for $M = Ir$, the first product of the reaction with HPF_6 is a cationic hydride which isomerises by migration of hydride to nbd and cleavage of the C_3-C_4 bond to form a η^2 -vinyl- η^3 -cyclopentenyl cation. The spectroscopic properties of these compounds will be compared with those recently reported on the related carborane nbd complexes by Hawthorne *et al.*²



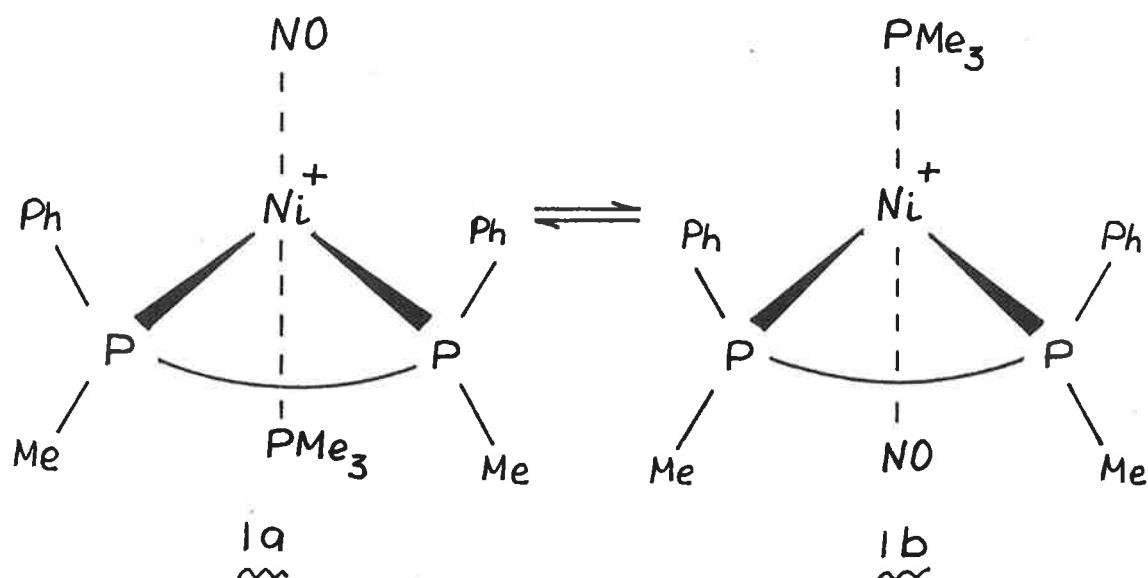
1. J. Evans, B.F.G. Johnson, and J. Lewis, J. Chem. Soc., Dalton Trans., 1977, 510.

2. D.M. Speckman, C.B. Knobler, and M.F. Hawthorne, Organometallics, 1985, 4, 1692.

REARRANGEMENTS IN NICKEL NITROSYL COMPLEXES

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Australian National University, Canberra, A.C.T. 2601.

The air-sensitive complex $[\text{Ni}(\text{NO})(\text{PMe}_3)\{(\underline{\text{R}}^*, \underline{\text{S}}^*)\text{-1,2-}\text{C}_6\text{H}_4(\text{PMePh})_2\}]\text{PF}_6$ exists in $\text{CH}_2\text{Cl}_2\text{-d}_2$ at 25°C as a 40:60 mixture of the diastereomers 1a and 1b, respectively. The slow recrystallization of the mixture from dichloromethane-ethanol mixture yields pure 1a in 70% yield (crystallization induced disequilibrium), which upon redissolution in $\text{CH}_2\text{Cl}_2\text{-d}_2$ transforms back into the original 40:60 mixture with $t_{1/2}$ ca. 40 min. at 10°C . The rearrangement is essentially intramolecular in nature, but there is a small intermolecular component as evidenced by the observation of $\text{PMe}_2\text{Ph}/\text{P}(\text{CD}_3)_2\text{Ph}$ exchange between the diastereomers of $[\text{Ni}(\text{NO})(\text{PMe}_2\text{Ph})\{(\underline{\text{R}}^*, \underline{\text{S}}^*)\text{-1,2-}\text{C}_6\text{H}_4(\text{PMePh})_2\}]^+$ and $[\text{Ni}(\text{NO})\{\text{P}(\text{CD}_3)_2\text{Ph}\}\{(\underline{\text{R}}^*, \underline{\text{S}}^*)\text{-1,2-}\text{C}_6\text{H}_4(\text{PMePh})_2\}]^+$ in $\text{CH}_2\text{Cl}_2\text{-d}_2$ at 25°C ($t_{1/2}$ ca. 12h at 25°C).



MULTINUCLEAR NMR STUDY OF REACTIONS OF AMINO ACIDS
 $^+NH_3(CH_2)_nCO_2^-$ AND AMINO-ALKYLPHOSPHONIC ACIDS
 $^+NH_3(CH_2)_nPO_3H^-$ WITH AMMINE COMPLEXES OF PLATINUM(II)

Trevor G. Appleton, John R. Hall, and Stephen F. Ralph

Department of Chemistry, University of Queensland

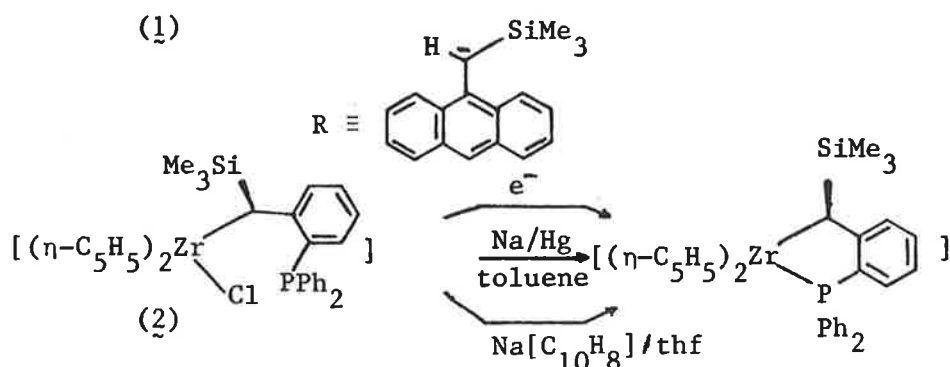
With the ammine N-atoms ^{15}N -substituted (>98%), multinuclear NMR allows characterization of the complexes formed in solution when these ligands react with ammine complexes of platinum(II). These reactions are profoundly affected by the length of the hydrocarbon chain in the ligand, n . For example, all of the ligands initially react with cis-Pt($^{15}NH_3$)₂(H₂O)₂²⁺ to give complexes with the ligand bound only through oxygen. Subsequent ring closure reactions to a N,O-chelate complex occur readily only for $n = 1$, and become progressively more difficult as n increases. In alkaline solutions, products of reactions are determined by the effect of n on the nucleophilicity of the amine group, as well as the decreasing tendency to form a chelate ring as n increases.

d¹ - Metal Alkyl Chemistry

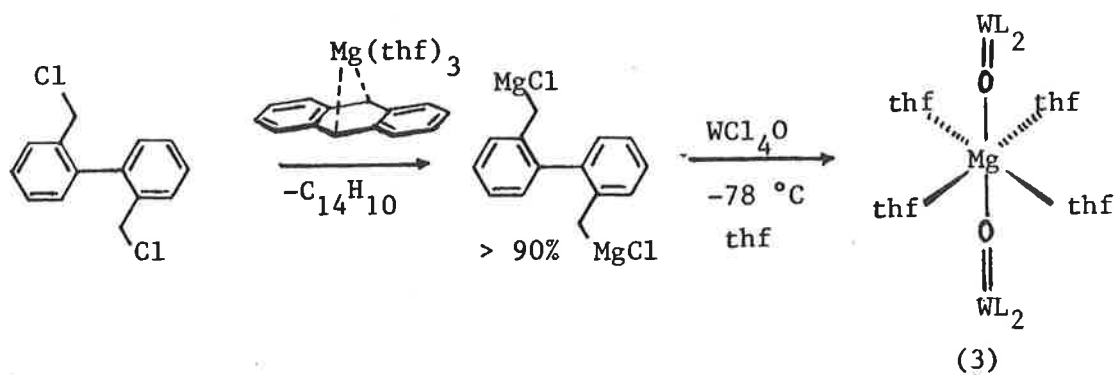
Lutz M. Engelhardt, Rocco I. Papasergio, Colin L. Raston, Geoffrey Salem, and Allan H. White.

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A., 6009.

Mononuclear d¹ alkyl metallocene complexes of zirconium tend to be rather reactive and kinetically unstable species and with a few exceptions there is some ambiguity relating to their structures. As part of a broad study of the synthesis, structure and reactivity of organozirconium(III) chemistry we have prepared a series of compounds bearing highly hindered alkyls, e.g. (1) and (2). By combining results from chemical and electrochemical studies coupled with e.s.r. data it is possible to assign structures with some certainty.



An unusual metal oxidation state of metal alkyl complexes is W(V). Instability here appears to be associated with tendency of W(V) to disproportionate. Reactions of the di-Grignard reagent derived from $[(2\text{-ClCH}_2\text{C}_6\text{H}_4)_2]$ and $\text{Mg}(\text{anthracene})(\text{thf})_3$ with WCl_4O in thf (= tetrahydrofuran) yields a stable paramagnetic species shown by an X-ray diffraction study to be (3). Within each molecule of (3) the bidentate alkyl ligands have the same chirality, the overall molecular symmetry being 222.



CORRELATION OF $\nu(\text{Fe-CO})$ WITH DISSOCIATION RATES FOR CARBONMONOXY -
DERIVATIVES OF MONOMERIC GLYCERA HEMEOGLOBINS - A RESONANCE RAMAN STUDY

R.S. Armstrong, B.J. Reedy, and M.J. Walsh

Department of Inorganic Chemistry, University of Sydney, N.S.W. 2006

P.E. Wright

Department of Molecular Biology, Research Institute of Scripps Clinic,
La Jolla, California 92037, U.S.A.

The hemoglobins of the marine annelid Glycera dibranchiata occur in both monomeric and polymeric forms, and exhibit strikingly fast association and dissociation rates for oxygen and carbon monoxide, as well as very low overall affinities for these ligands, relative to other hemeproteins.¹ The spectroscopic study of the oxy- forms of these proteins is made very difficult by their great sensitivity to oxygen, so in this work, the analogous CO-complexes have been studied, along with the five-coordinate deoxy-adducts, using resonance Raman (RR) spectroscopy.

With 457.9 nm and 406.7 nm laser excitation of the ^{12}CO and ^{13}CO complexes, the $\nu(\text{Fe-CO})$, $\nu(\text{C-O})$ and $\delta(\text{Fe-C-O})$ vibrational modes have been assigned to bands in the RR spectra of different monomeric Glycera hemoglobins - Band 4(III,C), Band 5 (II,B) and Band 6 (I,A) - all of which show marked differences in their CO- binding kinetics. An inverse correlation between Fe-CO bond strength and the rate of dissociation of the ligand (k_{off}) has been found. The associative rate constant, k_{on} , and the affinity, K , seem to be governed mainly by the protein environment of the heme. The relative intensities of the $\nu(\text{Fe-CO})$ and $\delta(\text{Fe-C-O})$ bands provide an indication of Fe-C-O distortion in the CO complexes.

Our studies of deoxy-Glycera hemoglobins indicate only slight differences in heme electronic structure between the three proteins. A band at about 220 cm^{-1} in the RR spectra of the deoxy-adducts has been assigned to the $\nu(\text{Fe-N}_{\text{E}})$ vibration.

1. Parkhurst, L.J. Sima, P., and Goss, D.H., Biochemistry, 1980, 19, 2688-2692.

METALLATION REACTIONS OF PHOSPHINES

N.K. Roberts

Department of Inorganic and Nuclear Chemistry,
University of New South Wales

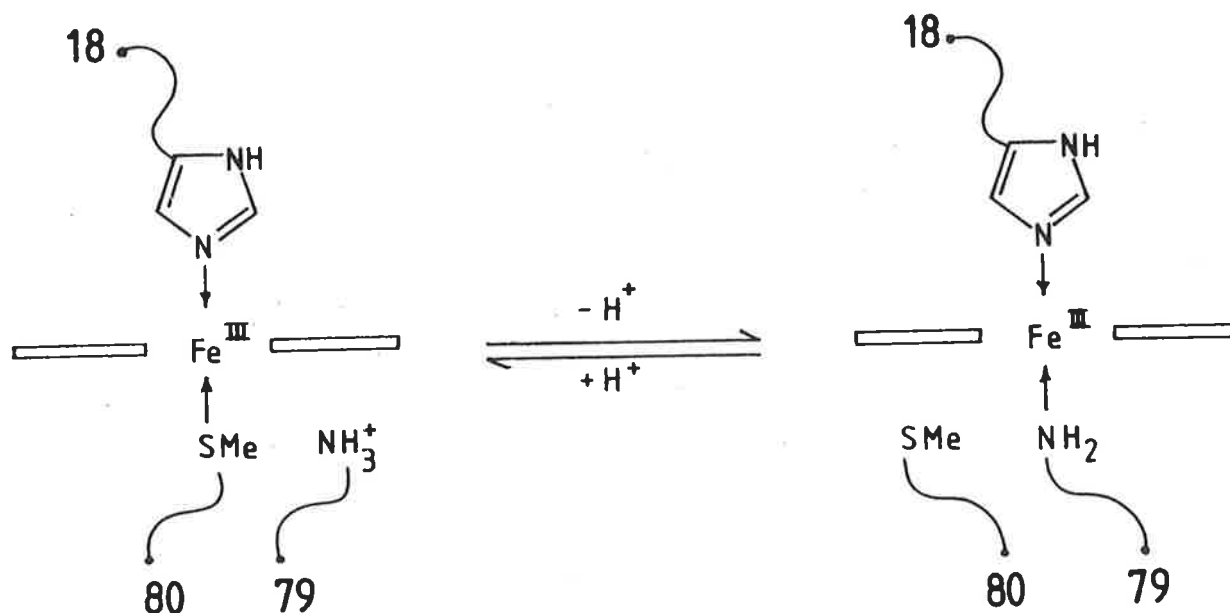
Simple tertiary phosphines such as PPh_3 and $\text{P}(\text{n-Bu})_3$ are used extensively as ligands in industrial processes such as hydroformylation. Few other phosphines of more elaborate structure are used commercially, except for the small scale production of high-value pharmaceutical substances.

An investigation has been made into the metallation reactions of simple phosphines of the type PhPR_2 , and into the subsequent elaboration of metallated species to more complicated phosphines.

ORIGIN AND RELATIONSHIP OF TWO ELECTROACTIVE FORMS OF CYTOCHROME c

by Clyde G. Rodrigues, Frank Farchione and Anthony G. Wedd
 Department of Chemistry, La Trobe University
 and Alan M. Bond, Division of Chemical and Physical Sciences,
 Deakin University.

The oxidised ferric form of the heme electron transfer protein cytochrome c exists in two protonation states ($pK \sim 8-9$) in aqueous bulk solution at pH 7-10:



Contrary to literature reports, both forms are redox active. The base form adsorbs preferentially on gold electrodes and a well-defined, irreversible reduction process is seen at -0.42 V vs SCE. The adsorption of the base form blocks the reversible pathway for the biologically-active acid form, which, however, is detected at $+0.01$ V in the presence of promoters such as I^- or 4,4'-bipyridyl. Adjustment of the proportion of protein and promoter permits both responses to be detected in the same solution and their ratio is pH-dependent. It is concluded that promoters facilitate electron transfer to the acid form at the expense of the base form by altering the position of protic equilibrium at the electrode surface.

**KINETICS OF REPLACEMENT BY CHLORIDE OF BIDENTATE CARBOXYLATE
LIGANDS CO-ORDINATED TO PLATINUM (II).**

I.A.G. ROOS and K.H. STOKES
Experimental Chemotherapy Unit
Cancer Institute
MELBOURNE 3000

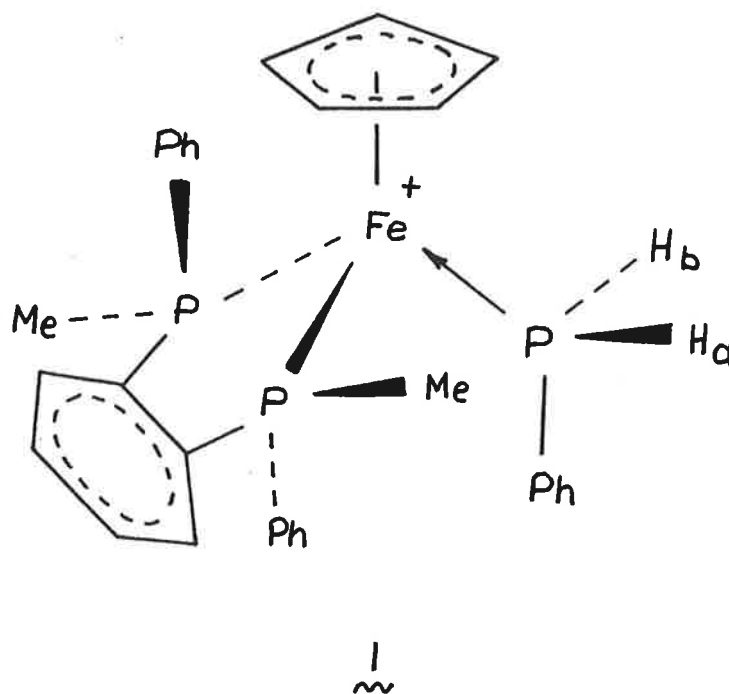
Following the successful use of the platinum complex, cis-diamminedichloroplatinum(II) as an anti-cancer drug, interest has focussed on obtaining other platinum compounds with clinically useful anti-tumour activity. Many of these "second generation" agents contain bidentate carboxylate ligands and whilst they are not as active as cis-platinum they have considerably useful agents. One explanation of their reduced toxicity is that they may act as "pro-drugs" with the carboxylate ligand being slowly replaced by chloride in serum. There is also interest in their uptake when given orally, where they would be exposed to low pH.

This study investigates the kinetics of replacement of carboxylate ligands by chloride at low and neutral pH. The reaction has been monitored by optical absorption at 300nm employing a micro-computer interfaced to the spectrophotometer. Five hundred data points were collected with the sampling interval being changed during the course of the reaction to maximise the precision of the data. In all cases two exponentials are observed with one contributing very little to the overall absorbance change. The data is consistent with a slow replacement of the carboxylate ligand to form a chloro complex, followed by slight hydrolysis.

STERESELECTIVITY OF ALKYLATION OF COORDINATED PRIMARY PHOSPHINES

Geoffrey T. Crisp, Geoffrey Salem, and S. Bruce Wild, Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601.

Complex 1, in which the PH protons are diastereotopic, is methylated in high yield in the presence of triethylamine to give a 4:1 mixture of two diastereomeric complexes containing coordinated methylphenylphosphine. The mixture has been separated by fractional crystallization and the major isomer has been characterised by X-ray crystallography. The subsequent alkylation of the pure diastereomers gives the same mixture of tertiary phosphine - containing diastereomers, regardless of which one is used as starting material, thus establishing that this reaction is proceeding under thermodynamic rather than kinetic control.



STEREOCHEMISTRY IN THE BIS(DIETHYLENETRIAMINE)CHROMIUM(III) CATION SYSTEM, $[\text{Cr}(\text{dien})_2]^{3+}$

Graeme H. Searle and Donald A. House

University of Adelaide, Adelaide, and University of Canterbury, Christchurch

In the cobalt(III) system $[\text{Co}(\text{dien})_2]^{3+}$, the three geometric isomers *mer*, *u-fac* and *s-fac* are readily separable from their preparative mixtures by cation-exchange chromatography, and have been thoroughly characterized.

For the analogous chromium(III) system $[\text{Cr}(\text{dien})_2]^{3+}$, all three geometric isomers would be expected to be capable of existence. However none of the yellow $[\text{Cr}(\text{dien})_2]^{3+}$ products reported by various workers has been isomerically characterized, so that the possible isomerism in this system has remained an intriguing problem since the first reported preparation in 1961 (Kling and Schläfer). Particular difficulties with chromium(III)-amine complexes are their tendency to hydrolyze via Cr-N bond rupture, their photosensitivity, and the uncertainty of effecting equilibrations.

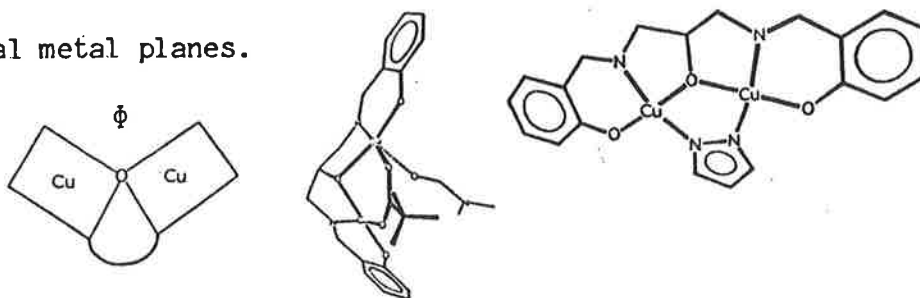
This stereochemical problem has now been clarified with our isolation and characterization of the *mer* and *s-fac* $[\text{Cr}(\text{dien})_2]^{3+}$ isomers. The *mer* is readily obtained (all the previous materials are *mer*). Hydrolysis of the *s-fac* is rapid, but this isomer has been crystallized in pure form as the $(\text{Hg}_2\text{Cl}_7)^{3-}$ and $(\text{ZnCl}_5)^{3-}$ salts. These two isomers are distinguished by their different labilities and spectra and by their different chromatographic behaviour, but these properties did not allow the isomeric structures to be assigned. The geometries were established from X-ray crystal structures of $[\text{Cr}(\text{dien})_2](\text{Hg}_7\text{Cl}_7)$ (Structures by Ward T. Robinson and Vickie McKee, University of Canterbury). The new isomers have been used to examine isomerization and cation-exchange chromatographic behaviour. The corresponding complex $[\text{Cr}(\text{dpt})_2]^{3+}$, with all six-membered rings, apparently can be obtained only as the *mer* isomer.

Cu(ACAC)₂ COMPLEXES WITH Fe(MAC)L AND Fe(MAC)X₂ (MAC = CONDENSATE OF PY-2,6-DIACETYL AND HYDRAZINE); COPPER AND IRON HOMO AND HETEROBINUCLEAR COMPLEXES INVOLVING Im, O AND PYRAZOLE BRIDGES.

Garry M. Mockler, Gary Erickson, U of Wollongong, Australia 2550; Greg A. Brewer, Ekk Sinn and Tom Sutto, University of Virginia, Charlottesville, Va 22901, USA

The ligand mac from pyridine-2,6-diacetyl and hydrazine forms ions of Type (1) Fe(mac)L²⁺ (L = bipyrimidine (Bpm), bpy) or Type (2) Fe(mac)X₂²⁺ (X = monodentate). Both types of ion complex with Cu(acac)₂, apparently via mac, to form a Cu-Fe binuclear. Type (1) forms mono-adducts whereas type (2) adducts two coppers. Steric constraints are a likely cause for the behavioral differences.

A more versatile binucleating method involves imidazole- and oxygen- containing Schiff base ligands, which coordinate to Cu and then bridge, via O or Im, to Fe-containing macrocycles. Two-sided Schiff base ligands can bridge two metals via a single oxygen, while allowing a variety of second ligands, such as carboxylates or pyrazole to be compared. The strength of magnetic coupling depends on the number of atoms in the bridging ligand and on the angle between the principal metal planes.



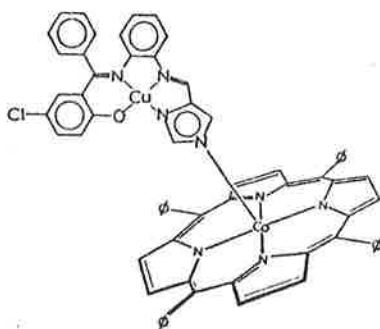
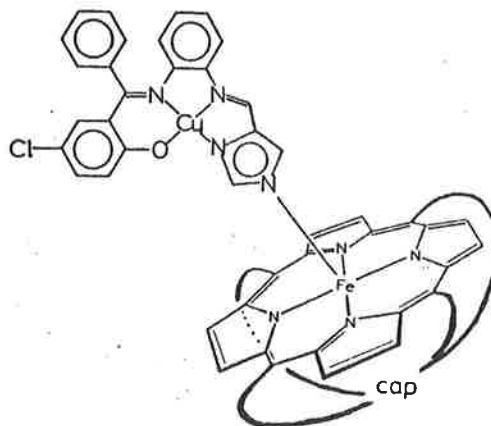
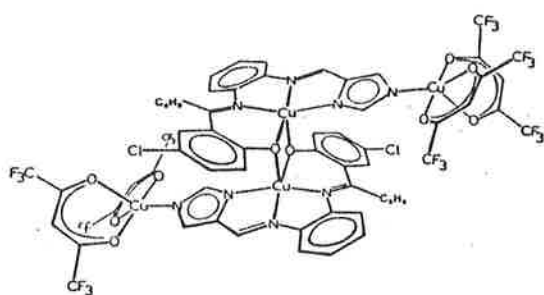
TETRANUCLEAR CU COMPLEXES WITH IMIDAZOLATES. THEIR STRUCTURES,
INTERACTIONS WITH OTHER METAL COMPLEXES; RELATION TO CYTOCHROME C
OXIDASE.

Odatt A. Rajan, Greg A. Brewer and Ekk Sinn

Department of Chemistry, University of Virginia, Charlottesville, Va
22901, USA.

The ligand H_2cbpIm forms complexes $[M(cbpm)]_2$ such as $[Cu(cbpm)]_2$ with approximately planar metal environments.

The imidazolate fragment can act as a Lewis base to bridge to appropriate Lewis acids, such as metal atoms bound to hexafluoroacetylacetonate (hfa) or to porphyrins. The adduct with $Cu(hfa)_2$ has two isomers. Both are tetranuclear, each containing two imidazole and two oxygen bridges. In the two isomers, the oxygen bridging involves different oxygen atoms. Binuclear complexes with $Cu(hfa)_2$, $Co(TPP)$ and $FeCl(TPP)$ are all antiferromagnetically coupled via imidazole bridge. The dimensions of such binuclear centers are compared with those of other related complexes.



STEPS II. PHOTOMAGNETISM OF TRANSITION METAL COMPLEXES.

Odatt A. Rajan, Fred C. Frederick, and Ekk Sinn
Department of Chemistry, University of Virginia,
Charlottesville, Va 22901.

Light-induced changes in the magnetic properties of a series of ferrous and ferric complexes have been investigated using STEPS (Susceptibility of Transient Excited Paramagnetic States). Irradiation of the complexes in a SQUID-based magnetometer at 15K produces excited spin states whose lifetimes are dependent on the oxidation state of the iron, the nature of the coordinated ligands, and the temperature of the sample after excitation. Results will be presented for complexes with temperature-independent and dependent (high spin-low spin) ground states.

Ab Initio Calculations on Sulphur Compounds II;
S-S Bonds in $S_2O_4^{2-}$, $S_2O_6^{2-}$ and S_2O_2 .

C.J.Marsden and B.J.Smith

Department of Inorganic Chemistry, University of Melbourne,
Parkville, Victoria 3052.

The disulphide linkage displays extraordinary variation in length and stiffness. Is its biological importance merely a coincidence? Consider the title compounds:

Dithionite, $S_2O_4^{2-}$, is doubly remarkable. In crystalline solids, it has an extremely long S-S bond (2.39 Å) and an unexpected eclipsed conformation. Our ab initio calculations successfully predict the long bond (2.40 Å), but suggest that for isolated anions, the trans conformation is more stable than the eclipsed by 45 kJ mol⁻¹. However, the calculations further show that binding of a cation is more favourable for the eclipsed form.

In the S(VI) oxyanion, $S_2O_6^{2-}$, the S-S distance of 2.16 Å is again successfully predicted by our calculations (2.17 Å). The $S_2O_6^{2-}$ ion makes much greater use of S d orbitals than does $S_2O_4^{2-}$, and this is one major factor leading to the shorter, stronger S-S bond; the s orbitals make a net bonding participation in $S_2O_6^{2-}$, whereas in $S_2O_4^{2-}$ their influence is S-S antibonding.

The sulphur oxide S_2O_2 has been identified so far only in the form cis planar OSSO. Although formally it contains an S=S double bond, the S-S distance is suprisingly long at 2.025 Å. Standard calculations predict a distance of only 1.931 Å, but once electron correlation is considered, the prediction of 2.039 Å is reasonably successful. Calculations further suggest that the trans form is almost equi-energetic with the cis, though only the cis form can be detected by microwave spectroscopy. A thio derivative of SO_3 is predicted to be almost 100 kJ mol⁻¹ more stable than OSSO, but cyclic structures do not seem favourable.

IS COPPER BOROHYDRIDE REALLY CuBH_4 ?

by Raymond J. Spokas and Bruce D. James

Department of Chemistry, La Trobe University,
Bundoora, Vic. 3083, Australia

While phosphine complexes of copper(I) borohydride are frequently used in organic chemistry¹ as reducing agents, little if anything is known about the thermally unstable species " CuBH_4 " prepared from a THF-ether solution of lithium borohydride and cuprous chloride². A detailed investigation carried out on this species, its decomposition products and complexes formed on addition of phosphine ligands revealed that the species actually exists in the form where both chloride and borohydride moieties are bound to copper.

1. G.W. Fleet, P.J.C. Harding and M.J. Whitcombe, Tet Letts., 21, 4031, (1980).
2. E. Wiberg and W. Henle, Z. Naturforsch. 7B, 582, (1952).

MOLYBDENUM BINDING BY *PSEUDOMONAS AERUGINOSA* PAO1by S. Stojkovski¹, R.J. Magee¹, V.A. Stanisich² and J. Liesegang³

Department of Chemistry¹, Department of Microbiology² and
 Department of Physics and Centre for Electron Spectroscopy³,
 La Trobe University, Bundoora, Victoria 3083, Australia

The uptake of Mo by certain bacteria hinders its role as a trace metal in the micronutrients for plant growth. The binding of Mo by the Gram-negative bacteria *Pseudomonas aeruginosa*, PAO1 has been investigated. A Mo complex of uronic acid, which forms in the extracellular polysaccharide layer (slime) was isolated and characterised by a variety of techniques. Comparisons with 'mimic' compounds of uronic acids suggest that *Pseudomonas aeruginosa*, PAO1 produces a binuclear, di-oxo-bridged magnesium salt: $\text{MgMo}_2\text{O}_4(\text{C}_6\text{H}_8\text{O}_7)_2 \cdot 5\text{H}_2\text{O}$, where $\text{C}_6\text{H}_8\text{O}_7$ is a glucuronate residue, thus indicating the important role of uronic acids in metallic uptake of bacteria.

SPIN TRANSITIONS IN IRON(II) COMPLEXES CONTAINING FIVE-MEMBERED HETEROCYCLES

Kristian H. Sugiyarto, Onggo Djulia and Harold A. Goodwin
School of Chemistry, University of New South Wales, P.O. Box 1
Kensington, N.S.W. 2033.

One of the iron(II) systems most suitable for detailed studies of the $^5T_2 \rightleftharpoons ^1A_1$ spin crossover in solution is $[\text{Fe}(\text{pyi})_3]^{2+}$ (pyi = 2-(pyridin-2-yl)imidazole) which displays a marked temperature and pressure dependence of its electronic spectrum under conveniently accessible experimental conditions. [J.J. McGarvey, I. Lawthers, K. Haremans, and H. Toftlund, *J.Chem.Soc.Chem.Comm.*, 1984, 1575; J. Di-Benedetto, V. Arkle, H.A. Goodwin, and P.C. Ford, *Inorg.Chem.*, 1985, 24, 455]. In the present work the corresponding iron(II) complexes of N-methyl-2-(pyridin-2-yl)imidazole, $[\text{Fe}(\text{mepyi})_3]^{2+}$, and N-methyl-2-(pyridin-2-yl)benzimidazole, $[\text{Fe}(\text{mepbi})_3]^{2+}$ have been prepared. A thermally induced singlet \rightleftharpoons quintet transition occurs in these systems but at higher temperatures than in the unsubstituted derivatives. For both of these systems the singlet state is principally populated at room temperature. Above room temperature an almost complete transition to the quintet state is observed for $[\text{Fe}(\text{mepbi})_3]^{2+}$ salts but for salts of $[\text{Fe}(\text{mepyi})_3]^{2+}$ an appreciable concentration of the low-spin species is still present, as indicated in the summary of the magnetic data given below. The reflectance spectra of the solid samples is significantly temperature-dependent.

Mössbauer data for both systems show the presence of both spin states at elevated temperatures and the singlet state only at low temperatures.

Salts of the previously unreported $[\text{Fe}(\text{2bt})_3]^{2+}$ ion (2bt = 2,2'-bithiazole) have also been prepared in this study. Previously [A.T. Baker, and H.A. Goodwin, *Aust.J.Chem.*, 1985, 38, 851] a spin transition was observed in $[\text{Fe}(\text{4bt})_3]^{2+}$ salts (4bt = 4,4'-bithiazole) but the system does not show the spectral properties typical for the iron(II) di-imine chromophore. $[\text{Fe}(\text{2bt})_3]^{2+}$ does, however, and also displays a temperature-induced spin transition which is accompanied by a strong temperature-dependence of the magnetism, Mössbauer and electronic spectra of its salts.

SUMMARY OF MAGNETIC DATA

System	μ at 90K	μ at 298K (B.M.)	μ at 363K
$[\text{Fe}(\text{mepyi})_3][\text{BPh}_4]_2$	1.34	1.71	2.09
$[\text{Fe}(\text{mepbi})_3][\text{BF}_4]_2$	0.96	3.26	4.88
$[\text{Fe}(\text{2bt})_3][(\text{ClO}_4)]_2$	2.31	5.03	-

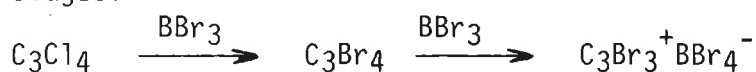
SOME REACTIONS AND STRUCTURAL STUDIES OF BORON HALIDES

Michael J. Taylor, Department of Chemistry,
University of Auckland, Auckland, New Zealand

Boron trihalides are noted Lewis acids, undergo facile exchange reactions, and can be induced to form diboron tetrahalides and higher polyborane compounds.

Structural data, especially Raman and I.R. spectra and vibrational assignments, will be presented arising from current investigations in this area:

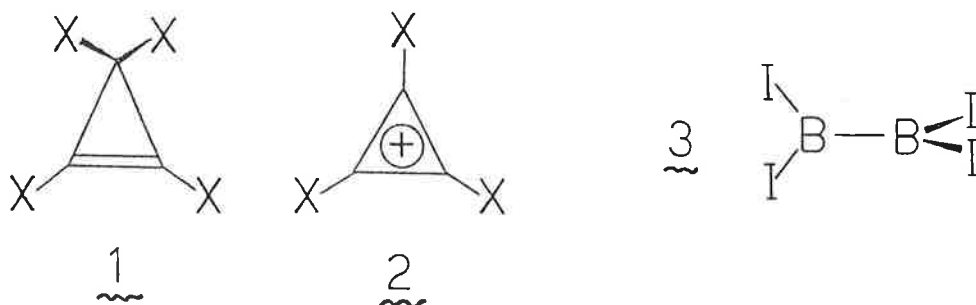
1. Simple Lewis acid-base adducts of BX_3 ($X = Cl, Br$ or I) with triphenylphosphine are compared with Group IIIB analogues, notably phosphine complexes of gallium trihalides.
2. Reactions of BX_3 with cycloheptatriene are a convenient route to crystalline tetrahaloborates, as the tropenium salts $C_7H_7^+BX_4^-$. These are being examined to extend previous structural analyses, including the characterisation of BBr_4^- and BI_4^- anions (with Robin Clark and Stephan Jost, University College, London).
3. Boron tribromide reacts with tetrachlorocyclopropene in two stages:



This process has been followed by Raman spectroscopy and ^{10}B N.M.R. The tribromocyclopropenium ion has been identified. The C_3X_4 molecules 1 and $C_3X_3^+$ ions 2 are of interest as prospective π -donor ligands for metal centres.

4. Diboron tetraiodide, pale yellow crystals obtained from BI_3 under radio-frequency discharge, gives an intense Raman spectrum which identifies it as possessing the staggered I_2B-BI_2 structure of D_{2d} symmetry 3 (like B_2Br_4 but unlike B_2Cl_4 and B_2F_4 , which are planar).

Other spectroscopic evidence suggests that the B_2I_4 molecule may be planar in the vapour phase and the need for further study of this apparently labile system is indicated.



HETEROCYCLIC DICATIONS DERIVED FROM THE TMEN LIGAND AND THEIR USE IN INVESTIGATIONS OF SOME INDIUM, ZINC, TIN AND MERCURY COMPLEXES

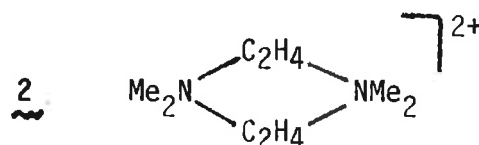
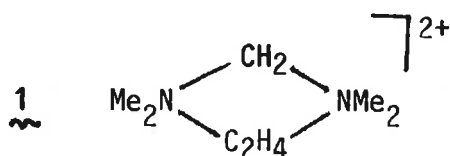
M.J. Taylor, G.R. Clark, and C.E.F. Rickard,
Department of Chemistry, University of Auckland, Auckland, New Zealand

Somewhat unexpectedly $\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2$ (tmen) reacts directly with CH_2Cl_2 or CH_2Br_2 to give the five-membered ring cation 1, and with $\text{BrC}_2\text{H}_4\text{Br}$ to give the six-membered ring 2.^a The reaction to form 1 has been encountered while preparing tmen complexes of Group III halides in a solvent system containing dichloromethane. The dications 1 and 2 are useful counterions for preparing crystals containing complex anions, ZnBr_4^{2-} , SnBr_6^{2-} etc.

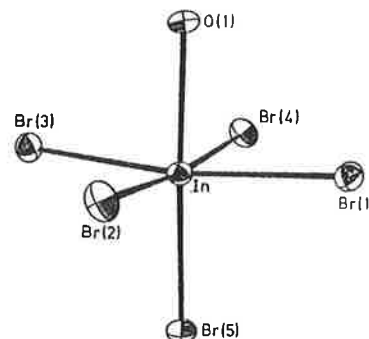
We have studied especially the systems formed by indium halides in aqueous solution as cases where an aquated cation $\text{M}(\text{OH}_2)_n^{a+}$ is progressively converted to halide complex anions with increased $[\text{X}^-]$. The bromide solution yields a crystalline product $\text{Me}_2\text{N}(\text{C}_2\text{H}_4)\text{NMe}_2 \cdot \text{InBr}_5 \cdot 2\text{H}_2\text{O}$ and the results of investigation by X-ray crystallography, and infrared and Raman spectroscopy will be shown.

The cation 2 is the N-tetramethylpiperazonium ion, which adopts the chair conformation of D_{2d} symmetry. The anion is six-coordinate $\text{InBr}_5\text{OH}_2^{2-}$ and a further solvent water molecule is hydrogen-bonded to this. Structural and spectroscopic comparisons of this species with other aquo-halogeno-complexes will be presented.

In further studies of the heterocyclic cations 1 and 2 we have found that the protons of the methylene group in the former, but not those of C_2H_4 groups, are labile, being exchanged for deuterium in the presence of a base. Dication 1 appears to undergo mercuration at this carbon atom, and this heterocycle is being investigated as a possible carbene precursor.



^aH. Noguchi and A. Rembaum, *Macromolecules* **5**, 253; 261 (1972).



ACID AND ANION ASSISTED DISSOCIATION OF THE COMPLEXES OF ZINC(II),
CADMIUM(II) AND MERCURY(II) WITH HEXAAMINE MACROBICYCLIC LIGANDS.

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¹Research School of Chemistry, Australian National University,
GPO Box 4, Canberra, A.C.T. 2601

²Department of Physical and Inorganic Chemistry, University of
Western Australia, Nedlands, W.A. 6009

The kinetics of the acid dissociation of the complexes of Hg(II), Cd(II) and Zn(II) with the ligands sar and diamsarH₂²⁺ have been examined in detail to try to elucidate how the metal ion is extruded from the cage.

For all complexes the rate of dissociation is strongly dependent upon acid concentration and the presence of coordinating anions. The kinetic data and ¹H NMR spectra allow a preliminary analysis of this mechanism. It can be seen that dissociation involves metal-nitrogen bond rupture followed by capture of the dissociated nitrogen by a proton. The exchange of amine protons in the complexes is indicative of the rate of this process. For [CddiamsarH₂]⁴⁺ the rate of proton exchange is slower than or equal to the rate of dissociation whereas for [ZndiamsarH₂]⁴⁺ proton exchange is faster than dissociation. It appears that, although the rate of metal-nitrogen bond rupture should not be significantly different to that found in the complexes of monodentate ligands, the relative rigidity of these ligands ensures that the nitrogen remains close to the metal ion resulting in a much faster return rate which leads to the high kinetic stability of these complexes.

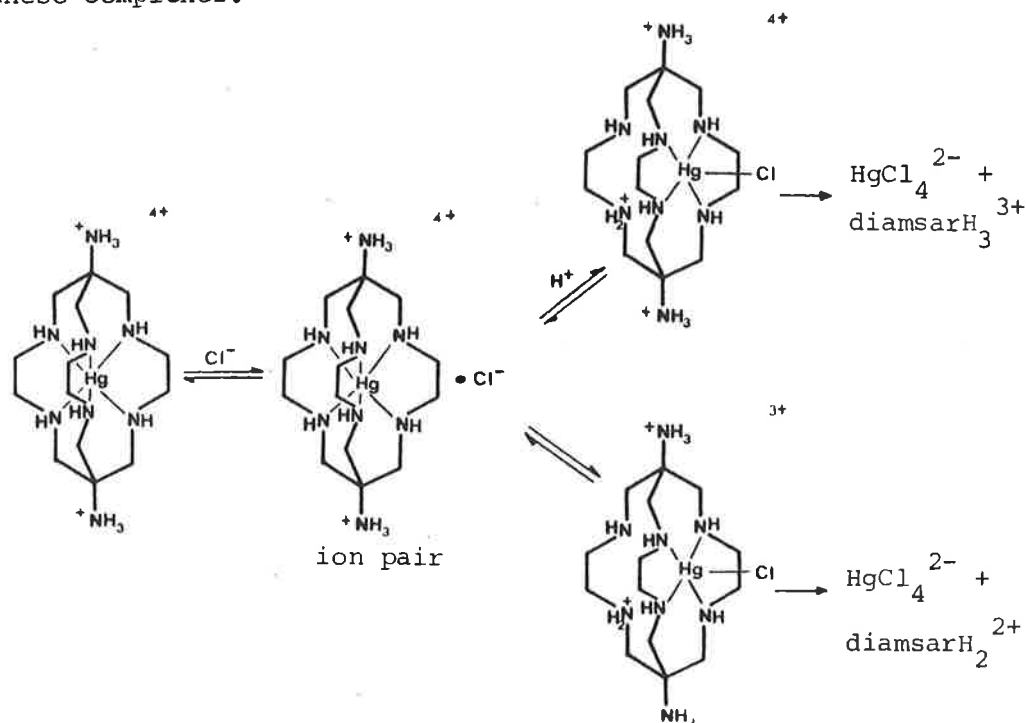


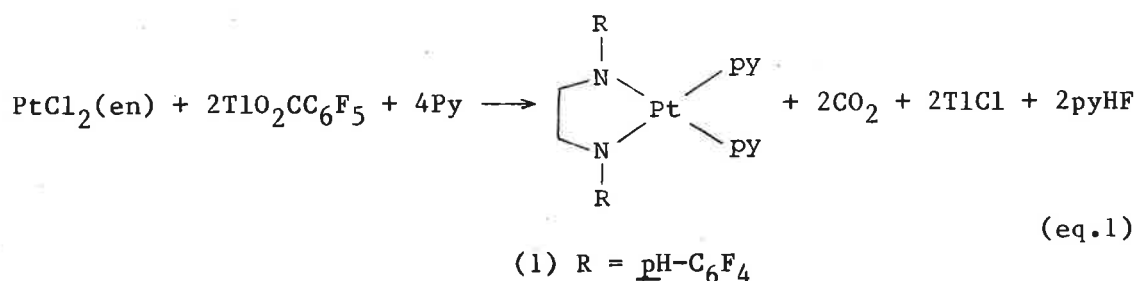
Figure: Route for the extraction of Hg²⁺ from [HgdiamsarH₂]⁴⁺ in acid in the presence of chloride.

SYNTHESIS AND STRUCTURES OF NOVEL ORGANOAMIDOPLATINUM(II) COMPOUNDS

D.P. Buxton, G.B. Deacon, B.M. Gatehouse, I.L. Grayson,
R.J. Thomson and P.J. Wright

Chemistry Department, Monash University, Clayton, Victoria 3168.

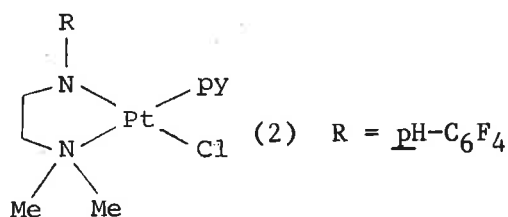
Decarboxylation reactions between PtCl_2L_2 (e.g. $\text{L}_2 = 2,2'$ -bipyridyl or *trans*-(pyridine)₂) complexes and thallous polyfluorobenzoates in boiling pyridine yield R_2PtL_2 (e.g. $\text{R} = \text{C}_6\text{F}_5$ or $\text{pH-C}_6\text{F}_4$) and RPtClL_2 organometallics.¹ However, the corresponding reaction of PtCl_2en (where en = ethane-1,2-diamine) with thallous pentafluorobenzoate does not give the expected $[(\text{C}_6\text{F}_5)_2\text{Pten}]$ or $[(\text{C}_6\text{F}_5)\text{PtCl(en)}]$ complexes but, rather, an N-(2,3,5,6-tetrafluorophenyl) substituted 1,2-diaminatoplatinum(II) complex (1) (eq.1).



A range of complexes of type (1) has been prepared with different substituents on the polyfluoroaromatic rings and also with several substituted pyridines.

The structure of (1) was established by X-ray crystallography.² An X-ray crystal structure of a similar complex containing two 2,4-dimethylpyridines is of interest as it shows the two substituted pyridines to be non-equivalent.

Reaction of $\text{PtCl}_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NH}_2)$ with thallous pentafluorobenzoate yields an analogous complex (2). The nature of the isomer obtained has recently been determined by X-ray crystallography.³ The halide is shown to be situated *trans* to the amido nitrogen.



1. Deacon, G.B. and Grayson, I.L., *Trans. Met. Chem.*, 1982, 7, 97.
2. Deacon, G.B., Gatehouse, B.M., Grayson, I.L. and Nesbit, M.C., *Polyhedron*, 1984, 3(6), 753.
3. Buxton, D.P., Deacon, G.B., Gatehouse, B.M., Grayson, I.L. and Wright, P.J., *Acta Cryst.*, 1985, C41, 1049.

ABSTRACTION OF SULFIDO LIGAND FROM $[\text{Mo}^{\text{VI}}\text{OS}]^{2+}$ AND RELATED CENTRES
BY CYANIDE

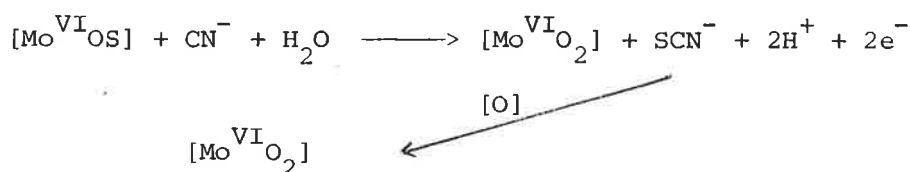
by Peter R. Traill, Maxwell J. O'Connor and Anthony G. Wedd

Department of Chemistry, La Trobe University

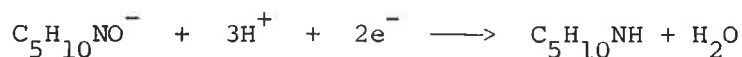
Molybdenum-containing hydroxylases such as xanthine oxidase (XO), xanthine dehydrogenase and aldehyde oxidase are inactivated by CN^- . An equivalent of SCN^- is released producing partially reduced enzyme with the electron equivalents distributed along the internal electron transfer chain (Mo , $2 \times \text{Fe}_2\text{S}_2$, flavin sites). Reoxidation furnishes the inactive "desulfo" enzyme:-



Interpretation in terms of the currently favoured model suggests:



The only well-characterised oxosulfidomolybdenum(VI) compounds are $[\text{MoOS}(\text{R}_2\text{NO})_2]$. The present work demonstrates that CN^- induces conversion of $[\text{MoOS}(\text{C}_5\text{H}_{10}\text{NO})_2]$ and $[\text{MoS}_2(\text{C}_5\text{H}_{10}\text{NO})_2]$ to $[\text{MoO}_2(\text{C}_5\text{H}_{10}\text{NO})_2]$ with liberation of SCN^- . The yield of $[\text{MoO}_2(\text{C}_5\text{H}_{10}\text{NO})_2]$ is about 50% and free $\text{C}_5\text{H}_{10}\text{NH}$ and $\text{C}_5\text{H}_{10}\text{NOH}$ are detected in solution. This suggests that the source of oxidising equivalents in this system is hydroxyl-amido ligand:-



AN IRON-ACTIVATED ALCOHOL DEHYDROGENASE

by Peter Tse, Robert K. Scopes and Anthony G. Wedd

Departments of Chemistry and Biochemistry,

La Trobe University

The well-characterised mammalian alcohol dehydrogenases (ADH) feature zinc at their active sites. The fermenting bacterium Zymomonas mobilis manufactures an iron-activated ADH (α_4 ; 148,000 d; one Fe per subunit) in addition to a zinc-activated enzyme (R.K. Scopes, FEBS Lett., 1983, 156, 303-306).

We have now developed a large scale (ca. 100 mg) isolation. The Fe-ADH is unstable as presently isolated (spec. act., 1000 IU/mg; half-life, 2 h), but we have found that isolation in the presence of Co^{2+} produces a more stable Co-substituted enzyme Co-ADH (spec. act., 400 IU/mg; half-life, >24 h). Significantly, demetallation of Co-ADH with 1,10-phenanthroline produces metal-free apo-enzyme which may be stored indefinitely at 77K and reactivated completely upon addition of stoichiometric Fe^{2+} or Co^{2+} .

Chemical and physical studies can now proceed conveniently. The former include measurement of metal binding constants and substitution of other metals, while the latter involve kinetics, electronic spectroscopy (vis-UV, CD, MCD), magnetic susceptibility, ESR and Mossbauer spectroscopy. Key points are that specific metal isotopes (e.g., ^{57}Fe for Mossbauer studies) can be inserted conveniently and that the metal-free apo-enzyme provides crucial control measurements (diamagnetic correction for magnetic susceptibility; reference background for electronic, ESR and Mossbauer spectroscopies).

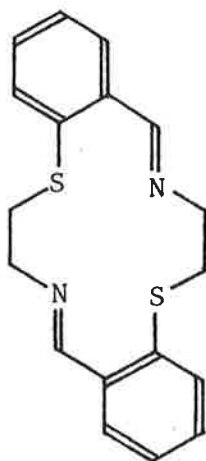
STABILIZATION OF COPPER(I) WITH A 14-MEMBERED TRANS-N₂S₂ MACROCYCLE

Kevin P. Wainwright

School of Physical Sciences, The Flinders University of South Australia,
Bedford Park, South Australia 5042.

The N₂S₂ donor atom arrangement is well known as a binding site for Cu in biological systems. Existing work¹ has shown that N₂S₂ macrocyclic ligands tend to stabilize Cu(I) complexes against aerobic oxidation in aqueous solution only when the macrocyclic ring consists of sixteen atoms; a ring size sufficiently flexible to accommodate the tetrahedral bond arrangement favoured by Cu(I).

By use of the smaller fourteen membered N₂S₂ macrocycle, (1), in which



(1)

the donor atoms are arranged trans, rather than cis, we now find that smaller rings are also capable of stabilizing Cu(I) in aqueous solution. Thus, addition of Cu(CH₃CN)₄ClO₄ to (1) in ethanolic solution precipitates bright orange needles of Cu(I)ClO₄, which are air stable and which when redissolved in water decompose only slowly over a period of days.

Since a fourteen membered ring is incapable of positioning its donor atoms in a tetrahedral arrangement it is likely that the Cu(I) is bound either with a distorted square-planar or possibly five co-ordinate geometry. The chemistry and electrochemistry of (1) and its reduced, diamine, form in conjunction with Cu(I) and Cu(II) will be fully described.

1. L. Siegfried and T.A. Kaden, Helvetica Chim Acta, 1984, 67, 29 & 1061.

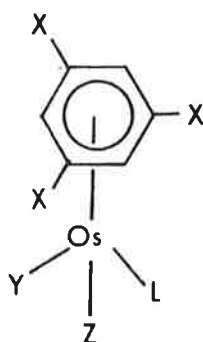
Chemistry of Mononuclear Arene-Osmium Complexes.

M.A. Bennett and A.M.M. Weerasuria.

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The 16-electron fragments $M(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)$ ($M=\text{Rh}, \text{Ir}$) generated by photolysis of $\text{MH}_2(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)$ and by other methods¹, have been shown to oxidatively add the C-H bonds of alkanes and arenes, whereas the isoelectronic fragment $\text{Ru}(\eta\text{-C}_6\text{Me}_6)(\text{PR}_3)$ adds arenes but not alkanes². Arene osmium(0) fragments $\text{Os}(\eta\text{-arene})(\text{PR}_3)$ can be expected to be even more reactive in oxidative addition and we are looking for routes by which such fragments could be generated. For this purpose we have prepared a series of mononuclear mesitylene-osmium and benzene-osmium complexes as shown below.



$\text{X}=\text{CH}_3$ or H

$\text{L}=\text{various tertiary phosphines}$

- a. $\text{Y}=\text{Z}=\text{Cl}$, dichloro derivatives
- b. $\text{Y}=\text{H}$, $\text{Z}=\text{Cl}$, monohydrido derivatives
- c. $\text{Y}=\text{Z}=\text{CH}_3$, dimethyl derivatives
- d. $\text{Y}=\text{Z}=\text{H}$, dihydrido derivatives

The formation of hydrido(methyl) and of cyclometallated arene-osmium complexes of the type $(\eta\text{-arene})\text{OsX}(\text{O-C}_6\text{H}_4\text{PR}_2)$ ($\text{X}=\text{H}, \text{Cl}$) will be discussed

1. (a). A.H. Janowicz and R.G. Bergman *J. Am. Chem. Soc.* 104, (1982), 352., 105, (1983), 3929. (b). W.D. Jones and F.J. Feher *J. Am. Chem. Soc.* 104, (1982), 4240. (c). W.D. Jones and F.J. Feher *Organomet.* 2, (1983), 562.
2. (a). H. Kletzin and H. Werner *Angew. Chem. Int. Ed. Engl.* 22, (1983), 873. (b). M.A. Bennett, Tai-Nang Huang and J.L. Latten *J. Organomet. Chem.* 272, (1984), 189.

OXIDATION OF SECONDARY AMINES COORDINATED TO RUTHENIUM(II)

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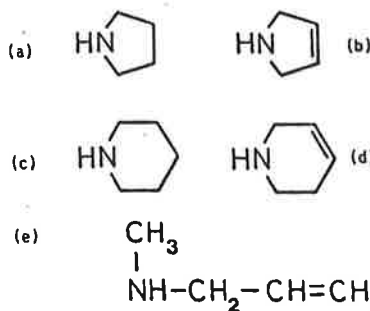
Department of Chemistry and Biochemistry

James Cook University of North Queensland

The oxidative dehydrogenation of isopropylamine in $(\text{tpy})(\text{bpy})\text{Ru}(\text{isopropylamine})^{2+}$ produces the corresponding monoimine complex but further oxidation can occur to yield $(\text{tpy})(\text{bpy})\text{Ru}=\text{N}=\text{CMe}_2^{3+}$.¹ In an attempt to synthesize complexes of monoimines but inhibit this subsequent reaction, we have now used secondary amines as the precursors.

The oxidation reactions of a series of secondary amines coordinated to Ru(II) , $(\text{tpy})(\text{bpy})\text{Ru}(\text{amine})^{2+}$, have been studied

where amine =



The amines pyrrolidine (a) and piperidine (c) underwent two-electron oxidations to yield complexes of the corresponding monoimines. Similarly, N-methylallylamine (e) underwent a two-electron oxidation to give a mixture of the exo- and endo-monoimines. NMR evidence will be presented to support the characterization of these products.

Amine (d) was oxidized (four electrons) to give the pyridine complex, whereas (b) apparently underwent decomposition and the oxo-ruthenium(IV) species was the major complex product.

Some aspects of the reactivity of the monoimine complexes derived from (a), (c) and (e) will be presented.

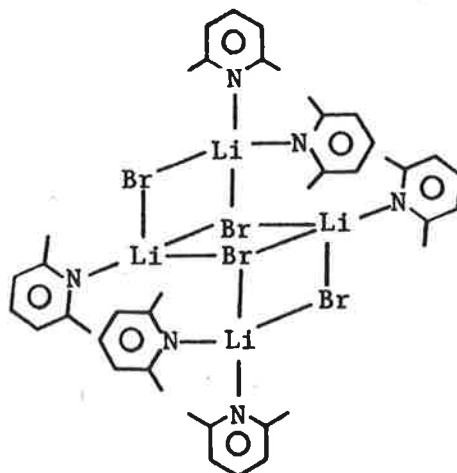
1. P.A. Adcock, F.R. Keene, R.S. Smythe, and M.R. Snow, *Inorg. Chem.* **23**, 2336 (1984).

Coordination Complexes of Lithium Halides with Amines

Colin L. Raston, Claire R. Whitaker, and Allan H. White.

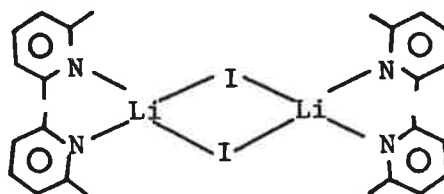
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A systematic study of complexes formed on treating lithium halides with N-centred Lewis bases has yielded two different structural types. For example, the 2,6-lutidine derivative of LiBr has a tetrameric 'step' structure in the solid, each lithium centre being four coordinate (1). In contrast, the LiI derivative is dimeric with bridging halides (2), as found in the structure of $[\text{LiBr}\{\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{NMe}_2\}_2]_2$, (3).¹ (c.f. $\text{Cu}_4\text{I}_6(\alpha\text{-picoline})_6$)².



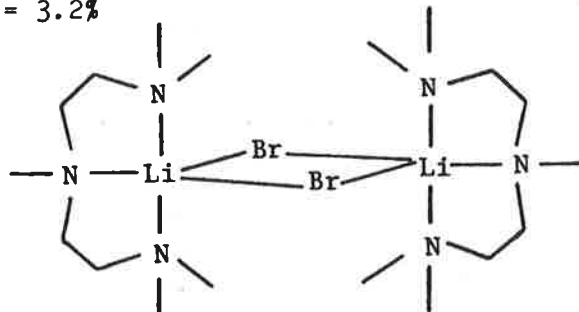
(1)

Space group $\bar{P}1$, $a = 13.020 \text{ \AA}$, $b = 12.191 \text{ \AA}$, $c = 8.265 \text{ \AA}$, $Z = 1$ tetramer. $R = 4.8\%$ (c.f. $\text{Cu}_2\text{I}_2(2,6\text{-lutidine})_2$)³



(2)

Space group $\bar{P}1$, $a = 11.023 \text{ \AA}$, $b = 10.024 \text{ \AA}$, $c = 8.352 \text{ \AA}$, $Z = 2$ dimers. Current $R = 3.2\%$



(3)

1. S.R. Hall, C.L. Raston, B.W. Skelton, and A.H. White, Inorg. Chem., 1983, 22, 4070-4073.
2. P.C. Healy, C. Pakawatchai, C.L. Raston, B.W. Skelton, and A.H. White, J. Chem. Soc., Dalton Trans., 1983, 1905.
3. J.A. Campbell, C.L. Raston, and A.H. White, Aust. J. Chem., 1977, 30, 1937.

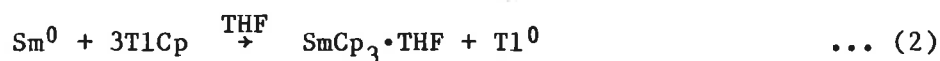
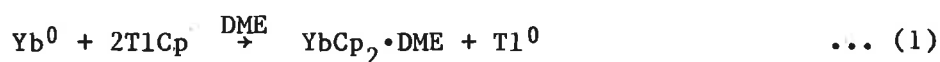
ORGANOLANTHANOID CHEMISTRY

G.B. Deacon, T.D. Tuong, D.L. Wilkinson, G.N. Pain, C.M. Forsyth,

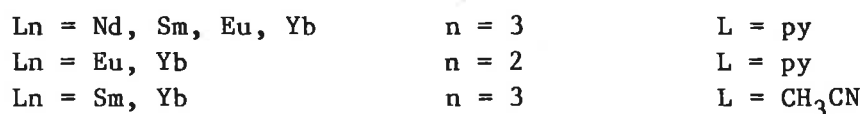
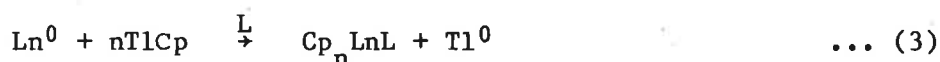
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Various divalent and trivalent organolanthanoid compounds have been prepared by transmetallation reactions between organomercurials or organothallium reagents and the lanthanoid metals. These preparations are usually carried out in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) [e.g. eq. 1,2]

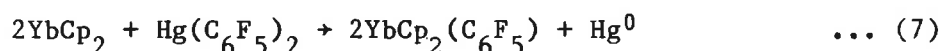
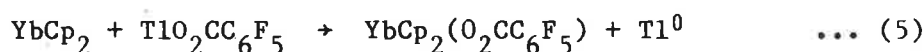
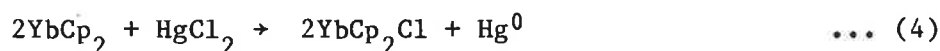


We now report the preparation of some cyclopentadienyllanthanoid compounds by transmetallation in pyridine and acetonitrile (eq. 3).



The use of pyridine as a solvent has enabled the formation of both tris(cyclopentadienyl)- and bis(cyclopentadienyl)europium with co-ordinated pyridine. Previously these compounds could not be synthesized by transmetallation using THF or DME as solvents.

The preparation of bis(cyclopentadienyl)(1,2-dimethoxyethane)-ytterbium(II) by transmetallation (eq. 1) also offers a convenient route to $\text{YbCp}_2(\text{X})$ compounds via oxidation reactions. Reaction with a number of metal salts has been observed. Bis(cyclopentadienyl)-ytterbium-carboxylates, -halides, - β -diketonates and other organo-metallic species have been prepared (eg. eqs. 4,5,6,7).



Some X-ray crystallographic studies have also been carried out.

STRUCTURAL CHEMISTRY OF NITRIDO COMPLEXES OF TECHNETIUM

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The nitrido ligand (N^{3-}) is a powerful π -electron donor which may act as a terminal or bridging ligand and which tends to stabilise metals in high oxidation states. With terminal nitrido ligands, the formal metal-nitrogen bond order corresponds to a triple bond, and crystal structure determinations of nitrido complexes manifest extremely short metal-nitrogen bond lengths and the distinct trans-effect of the π -bonded nitrogen ligand. Previous work has shown that mononuclear nitrido complexes are most readily formed by the metals molybdenum, ruthenium, tungsten, rhenium and osmium, with osmium forming the most extensive and stable series of nitrido complexes.

We reported the first nitrido complex of technetium in 1981, and the crystal structure determination of $[\text{TcN}(\text{S}_2\text{CNEt}_2)_2]$ confirmed the presence of a short $\text{Tc}\equiv\text{N}$ bond of length 1.604(6) Å. Since 1981, we have determined the crystal structures of five mononuclear nitrido complexes of technetium containing $\text{Tc}\equiv\text{N}$ bonds.

$\text{Tc}\equiv\text{N}$ bond distances range from 1.581(5) and 1.596(6) Å in the technetium(VI) complexes of the air-stable tetraphenylarsonium salts of the $[\text{TcNCl}_4]^-$ and $[\text{TcNBr}_4]^-$ anions, to 1.623(4) Å in the square-pyramidal technetium(V) nitrido complex of the 8-quinolinethiol (thiooxine) ligand, $[\text{TcN}(\text{C}_9\text{H}_6\text{NS})_2]$, and 1.629(4) Å in the distorted octahedral technetium(V) complex $[\text{TcN}(\text{NCS})_2(\text{CH}_3\text{CN})(\text{PPh}_3)_2]$. In this latter compound, the strong trans influence of the nitrido ligand is evident in the exceptionally long $\text{Tc}-\text{N}$ bond distance of 2.491(4) Å to the CH_3CN ligand.

It is apparent that the $\text{Tc}\equiv\text{N}$ bond, in the complexes studied to date, possesses an unusual stability at least equivalent to that found with osmium-nitrido complexes.

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Abstract

The kinetics and mechanism of the reduction of oxidised cytochrome c by ascorbate has been investigated in potassium nitrate, potassium 2-morpholinoethanesulfonate (KMES), potassium sulfate and potassium ascorbate media. The results are consistent with simple second order electron transfer from ascorbate dianion to cytochrome c and do not support electron transfer from an ascorbate dianion bound to the protein of the cytochrome as recently proposed by Myer and Kumar. A rate constant of $8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (25°C, ionic strength 0.1) was found for the electron transfer step. This rate constant is essentially independent of the specific ions used in controlling ionic strength.

MULTIFREQUENCY ESR OF MOLYBDENUM(V) CENTRES: SYNTHETIC SPECIES AND
THE ENZYME XANTHINE OXIDASE

by Graham L. Wilson, Graeme R. Hanson, Trevor D. Bailey,
John R. Pilbrow and Anthony G. Wedd.
La Trobe and Monash Universities.

While isotope (^2H , ^{13}C , ^{17}O , ^{33}S) substitution studies have proven valuable in mechanistic studies of various molybdo-enzymes¹, detailed interpretation of Mo and W ESR data from such systems is often difficult due to low symmetry sites where the g-tensor, A-tensor and molecular principal axes are not aligned, in general. Examination of the ESR spectra as a function of frequency (2,3,4,9 GHz), coupled with spectral simulation and isotope substitution, allows a concerted attack on the problem.

Our approach is to examine intensively a series of synthetic Mo(V) and W(V) species of increasing spectral complexity culminating in the enzyme xanthine oxidase:-

- (a) $[\text{Mo}(\text{abt})_3]^-$ ($\text{abtH}_2 = o\text{-aminio benzenethiol}$): isotropic g-tensor, anisotropic A-tensor.
- (b) $[\text{MO}(\text{XPh})_4]^-$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}$): axial system with $\text{A}(^{183}\text{W})^-$, $\text{A}(^{17}\text{O})$ and $\text{A}(^{77}\text{Se})$ -tensors revealed at low frequencies.
- (c) $[\text{MoOCl}(\text{mq})_2]$ ($\text{mqH} = \text{quinoline-8-thiol}$): lower frequencies reveal an axial system with $^{35,37}\text{Cl}$ coupling.
- (d) $[\text{MoO}(\text{MeOH})(\text{salen})]^+\text{Br}^-$: a rhombic system.
- (e) Xanthine oxidase: ^{95}Mo -substitution permits examination of the ^{95}Mo -coupling as a function of frequency.

1. R.C. Bray in "Biological Magnetic Resonance", Vol. 2, 45 (1980).

Some reactions of the iron(II) *meso*-tetraphenylporphyrin dichlorocarbene complex $\text{Fe}(=\text{CCl}_2)(\text{TPP})$ with nucleophiles.

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It has been shown that complexes containing the dichlorocarbene ligand can serve as versatile synthetic intermediates. The complex $\text{OsCl}_2(=\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$, for example, reacts with primary amines, aryl lithium reagents, thiols and hydrogen chalcogenides to form compounds containing coordinated isocyanides, carbynes, thiocarbenes and chalcocarbonyls respectively.^{1,2} In most cases reaction is thought to proceed via nucleophilic attack at C(carbene) followed by loss of chloride substituents.

The iron(II) *meso*-tetraphenylporphyrin dichlorocarbene complex $\text{Fe}(=\text{CCl}_2)(\text{TPP})$ was first reported by Mansuy *et al.* in 1977.³ The dichlorocarbene ligand in this molecule has been reported to react readily with primary amines to yield coordinated isocyanides.⁴ We have been investigating reactions of this complex with other nucleophiles to determine if any further similarities in reactivity are shared by $\text{OsCl}_2(=\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$ and this complex. We have found that reaction of $\text{Fe}(=\text{CCl}_2)(\text{TPP})$ with SeH^- produces the expected selenocarbonyl complex $\text{Fe}(\text{CSe})(\text{TPP})$ in good yield. Reaction with TeH^- , however, is more complex and one of the products of this reaction is the previously reported μ -carbido dimer $(\text{TPP})\text{Fe} = \text{C} = \text{Fe}(\text{TPP})$. Further details of these and other related reactions will be presented.

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- ³D. Mansuy, M. Lange, J.C. Chottard and P. Guerin, J.C.S. Chem. Comm., 1977, 648.
- ⁴D. Mansuy, M. Lange, J.C. Chottard and J.F. Bartoli, Tetrahedron Letters, 1978, 33, 3027.

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