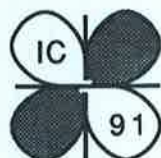


# PART 2



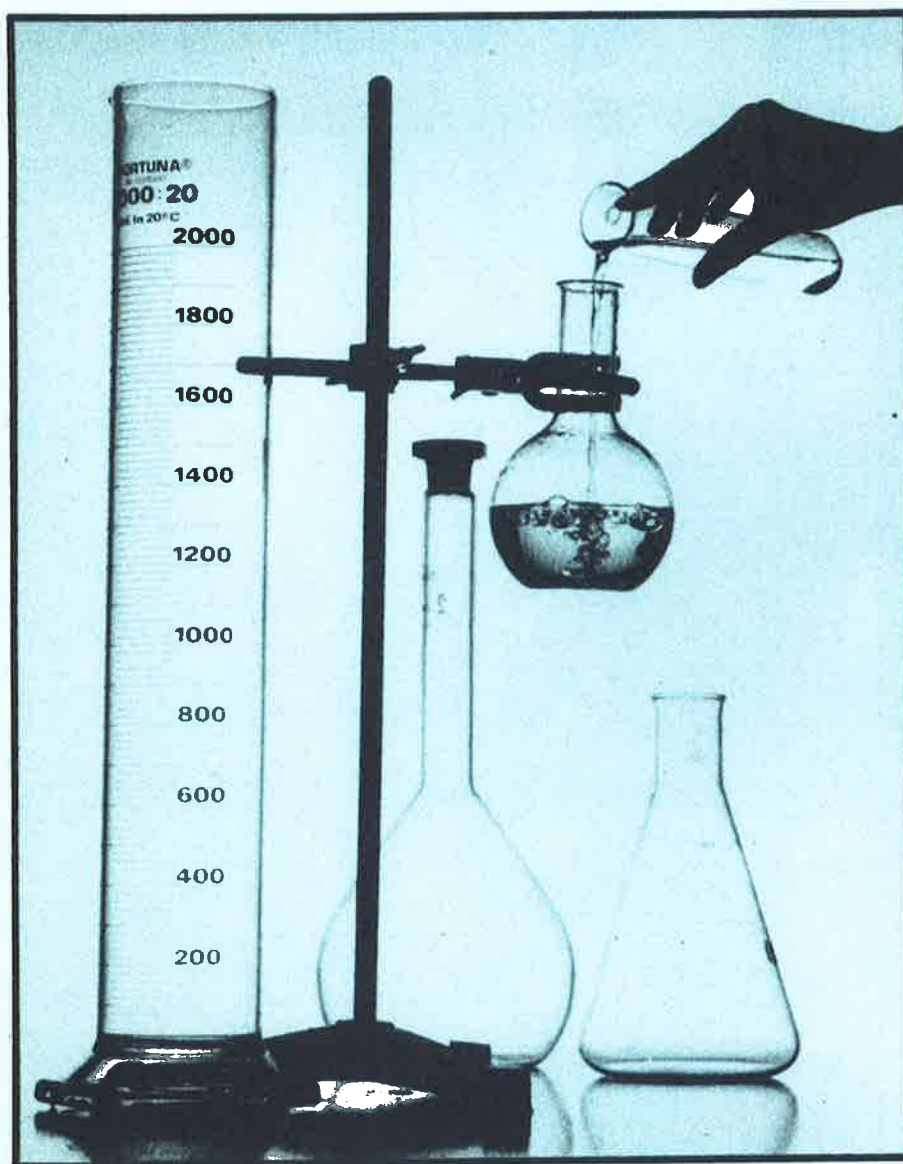
WAIKATO  
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## Inorganic Chemistry '91

Conference of the RACI Inorganic Division and the  
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UNIVERSITY OF WAIKATO, HAMILTON, NEW ZEALAND.

JANUARY 28TH TO FEBRUARY 1ST, 1991

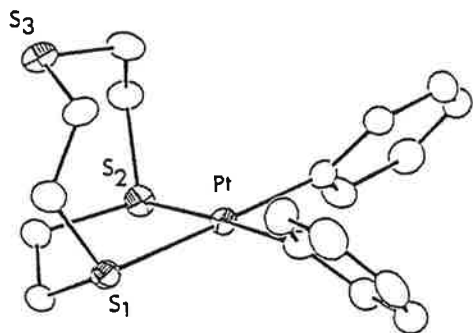
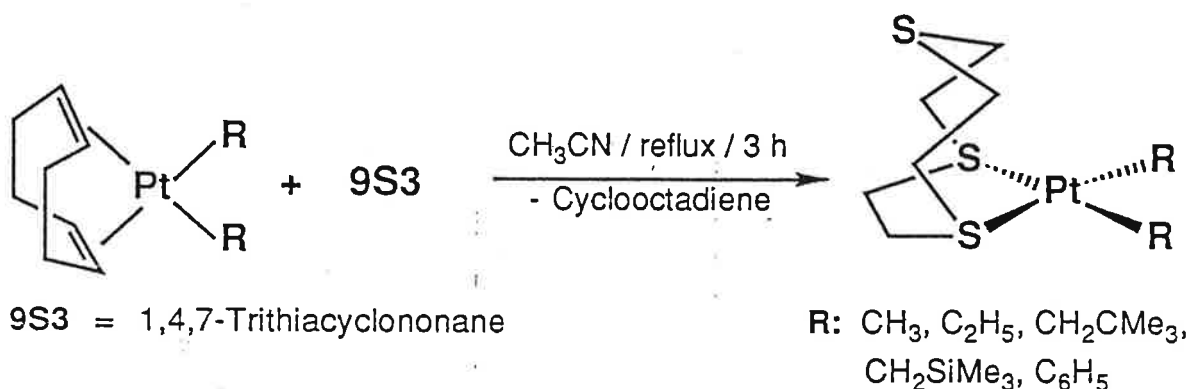


# Synthesis, Structure and Reactions of (1,4,7-Trithiacyclononane)platinum Alkyl Complexes

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A novel series of neutral alkylplatinum(II) complexes with the empirical formula  $(9S3)PtR_2$  is obtained by replacement of cyclooctadiene from corresponding  $(COD)PtR_2$  complexes in high yield. The compounds are fully characterized by IR-, NMR-, mass-spectroscopy and elemental analysis.



The X-ray analysis of  $R = C_6H_5$  reveals a distorted square planar configuration around the platinum centre. Only two sulfur atoms of the thia crown ether are coordinated to the metal. This seems to be the first complex with a single, exodentate 9S3-ligand.

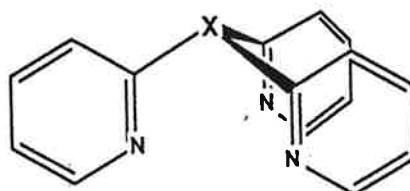
Treatment of  $(9S3)PtR_2$  with  $CH_3I$  or  $X_2$  ( $X = Br, I$ ) gives quantitatively the pseudo-octahedral  $Pt(IV)$  oxidative addition products  $[(9S3)PtR_2(CH_3)]^+[I]^-$  and  $(9S3)PtX_2R_2$ .

AMBIDENTATE COORDINATION OF THE TRI-PYRIDYL LIGANDS  
2,2':6',2''-TERPYRIDYL, TRIS(2-PYRIDYL)AMINE,  
TRIS(2-PYRIDYL)METHANE, AND TRIS(2-PYRIDYL)PHOSPHINE TO  
CARBONYLRHENIUM CENTRES

Peter A. Anderson,<sup>a</sup> F. Richard Keene,<sup>a</sup> Ernst Horn,<sup>b</sup> and Edward R.T. Tiekink<sup>b</sup>

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$\text{py}_3\text{X}$  {X = N, CH, P}

The reaction of  $[\text{Re}(\text{CO})_5\text{Cl}]$  with the ligands tpy (2,2':6',2''-terpyridine),  $\text{py}_3\text{N}$  {tris(2-pyridyl)amine},  $\text{py}_3\text{CH}$  {tris(2-pyridyl)methane}, and  $\text{py}_3\text{P}$  {tris(2-pyridyl)phosphine} in toluene solution realises compounds with the general formulation  $[\text{Re}(\text{ligand})(\text{CO})_3\text{Cl}]$  in which the tri-pyridyl ligands are bidentate. X-ray structural determinations of *fac*- $[\text{Re}(\text{tpy})(\text{CO})_3\text{Cl}] \cdot \text{H}_2\text{O}$  and *fac*- $[\text{Re}(\text{py}_3\text{N})(\text{CO})_3\text{Cl}]$  confirm these assignments. If the synthetic procedure is undertaken under irradiation by visible light, for the ligands  $\text{py}_3\text{N}$ , a species  $[\text{Re}(\text{py}_3\text{N})(\text{CO})_2\text{Cl}]$  (characterised by infrared spectroscopy and conductance measurements) is also formed in which the ligand  $\text{py}_3\text{N}$  is tridentate. A similar result is observed for the ligand  $\text{py}_3\text{CH}$ . No analogous tridentate species is formed with the ligands tpy or  $\text{py}_3\text{P}$ .

**SUPRAMOLECULAR TRANSPORT OF METAL COMPLEXES.  
CHIROSELECTIVE MEMBRANE TRANSPORT OF METAL AMINE  
COMPLEXES BY A POLYETHER IONOPHORE, LASALOCID A**

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The naturally occurring polyether antibiotic, lasalocid A, has recently been demonstrated to act as an ionophore for the transport of the hexamminecobalt(III) ion across a chloroform membrane.<sup>1</sup> "Uphill" transport was achieved against a counter gradient of ammonium ions such that it was possible to drive the transfer of the cobalt complex to completion - that is, from the aqueous source phase to the aqueous receiving phase. The evidence suggests that transport involves the formation of a 3:1 outer sphere complex between lasalocid (in a cyclic conformation) and the cobalt complex which is largely held together by a network of hydrogen bonds.

In an extension of the above study lasalocid A has been demonstrated to act as an ionophore for the selective enantiomeric transport of the amine-containing metal complex cations  $[\text{Co}(1,2\text{-diaminoethane})_3]^{3+}$ , *u-cis*- $[\text{Co}(\text{diethylenetriamine})_2]^{3+}$  and  $[\text{Co}(\text{sepulchrates})]^{3+}$  across a chloroform membrane. Partial resolution of the racemic mixture of each of these cations originally in the aqueous source phase was found to have occurred in the aqueous receiving phase after the respective transport experiments had proceeded for 6 hours. Under the conditions employed, the enantiomeric excess in the receiving phase was 10% for the complex of 1,2-diaminoethane and 27% for that of diethylenetriamine (after 6 hours). These latter results represent an important development - the first report of transport experiments being used to obtain chiral discrimination between the optical isomers of a metal complex. The results also represent both a novel extension within the area of host guest chemistry as well as pointing the way for the use of transport behaviour for the separation and/or sensing of metal complexes.

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<sup>1</sup>L. F. Lindoy, G. W. Walker, and G. W. Everett, *J. Am. Chem. Soc.*, 1990, **112**, 3659.

## NEW CATION SENSORS BASED ON MIXED-DONOR MACROCYCLES

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Cation-selective membrane electrodes have been constructed using mixed oxygen-nitrogen donor macrocycles. In a previous investigation, the macrocycles have been demonstrated to yield complexes which do not show the extreme kinetic inertness characteristic of some macrocyclic systems incorporating only nitrogen donors.<sup>1</sup>

In the present study each macrocycle of interest was incorporated into a P.V.C. film containing plasticiser [di(2-ethylhexyl)sebacate] to produce a membrane; this was then used to prepare an electrode for quantitatively sensing particular metal and/or organic cations. For many systems a quasi Nernstian response was observed.

A typical study involved the sensing of guanidinium thiocyanate. In this case a linear response over the range  $10^{-1}$  mol dm<sup>-3</sup> to  $10^{-4}$  mol dm<sup>-3</sup> was observed with a detection limit of  $10^{-5}$  mol dm<sup>-3</sup>.

In other studies useful metal-ion selectivity occurred which paralleled that observed previously for the particular macrocycle under investigation.

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<sup>1</sup>L. F. Lindoy, "Heavy Metal Chemistry of Mixed Donor Macrocyclic Ligands: Strategies for Obtaining Metal Ion Recognition", Ch. 2, in *Synthesis of Macrocycles* eds. R. M. Izatt and J. J. Christensen, Wiley, New York, 1987.

## O<sub>2</sub>N<sub>2</sub>-DONOR MACROCYCLES IMMOBILISED ON SILICA GEL: Ni(II)/Cu(II) SELECTIVITY BASED ON KINETIC DISCRIMINATION

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The use of macrocyclic ligands to achieve metal-ion discrimination has been well documented.<sup>1</sup> In previous studies in our laboratory structural, thermodynamic, and kinetic aspects of the complexation of a series of 15- to 17-membered O<sub>2</sub>N<sub>2</sub>-donor macrocycles with Co(II), Ni(II), Cu(II), and Zn(II) have been investigated.<sup>2</sup> It was found that, for each cyclic system, the thermodynamic stabilities towards these ions follow the Irving-Williams series [with the Cu(II) complex showing the highest stability in each case]. In contrast, the Ni(II) complexes were found to be more kinetically stable than their Cu(II) analogues.

In order to use the observed kinetic behaviour as a basis for separating selected ions, we have chemically bound<sup>3</sup> the above macrocycle to a derivatised silica gel substrate. The use of such immobilised reagents in a two phase system has been found to facilitate the separation process. In general, the observed thermodynamic and kinetic characteristics of immobilised ligands parallel those of the free macrocycles. Even though Cu(II) is thermodynamically bound more strongly than Ni(II) to the functionalised surface, it is preferentially released before Ni(II) when exposed to acidic conditions. In this manner separation which is not dictated by the usual Irving-Williams restraints has been possible.

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<sup>1</sup>L. F. Lindoy, "The Chemistry of Macrocyclic Ligand Complexes", Cambridge University Press, Cambridge, U.K. 1989.

<sup>2</sup>G. Anderegg, A. Ekstrom, L. F. Lindoy, and R. J. Smith, *J. Am. Chem. Soc.*, 1980, **102**, 2670; L. F. Lindoy, H. C. Lip, J. H. Rea, R. J. Smith, K. Henrick, M. McPartlin, and P. A. Tasker, *Inorg. Chem.*, 1980, **19**, 3360; K. R. Adam, G. Anderegg, L. F. Lindoy, H. C. Lip, M. McPartlin, J. H. Rea, R. J. Smith, and P. A. Tasker, *Inorg. Chem.*, 1980, **19**, 2956.

<sup>3</sup>V. Dudler, L. F. Lindoy, D. Sallin, and C. W. Schlaepfer, *Aust. J. Chem.*, 1987, **40**, 1557.

## Molecular Mechanics Study of Nickel(II) Complexes of Macrocycles

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and Leonard F. Lindoy

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MOLMEC, a new molecular mechanics package, has been developed at James Cook University. The package incorporates the following programs: (a) MOLMIN minimizes the molecular geometry of a structure, using a quasi-Newton minimisation algorithm and a BFGS update method with analytical first derivatives; (b) ANAL analyses a structure in terms of its component elements of strain. It produces a listing of the bond lengths, bond angles, van der Waals' interactions, dipole-dipole interactions, out-of-plane distances and torsional. Strain energy contributions from each of these interactions and the total strain energy of the structure are also listed; (c) COMPAR compares two structures containing the same number and types of atoms. It lists the respective bond lengths, bond angles, out-of-plane angles, and torsion angles as well as the differences between them. Such a listing is useful for estimating the match (or otherwise) between an X-ray structure and the corresponding calculated structure after minimisation with MOLMIN; (d) ADATOM scans a file of atom coordinates for a structure and adds H atoms or lone pairs of electrons to C, N, O or S atoms when required. This program is useful for adding H atoms to X-ray structures that are often not reported in the literature; (e) HOLPLN calculates the hole size of the ligand cavity for a given structure. It also calculates least squares planes and atom deviations from the calculated planes.

With this package we have extended the Allinger MM2 force field for use with macrocyclic complexes of Ni(II). Although molecular mechanics investigations of particular Ni(II) complexes of macrocycles have been performed previously, no calibration of the force field over an extended series of complexes has yet been reported. X-ray data for twenty six low spin Ni(II) complexes have been used in the calibration of the extended force field. Inclusion of an out-of-plane bending term, which restricts the degree to which the Ni(II) atom can deviate from the least squares plane of the donor atoms, was generally beneficial in modelling the respective coordination planes. Twenty four X-ray structures of high spin Ni(II) complexes were also used to further extend the force field to include high spin Ni(II).

The application of the extended force field to (i) the investigation of the configurational isomers of selected Ni(II) complexes and (ii) the prediction of structure/function relationships in metal-ion recognition studies involving macrocyclic systems has been carried out.

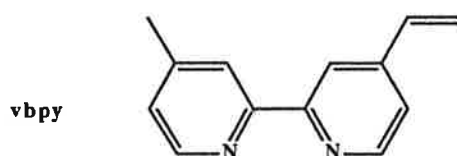
# ELECTROPOLYMERIZATION OF 4-METHYL-4'-VINYL-2,2'-BIPYRIDINE PROMOTED BY TRANSITION METAL CENTRES: STUDIES OF THE NATURE OF THE POLYMER FILMS USING LASER DESORPTION TECHNIQUES

Laurence S. Kelso,<sup>a</sup> Ian M. Atkinson,<sup>a,b</sup> Alan E.W. Knight,<sup>b</sup> and F. Richard Keene<sup>a</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Queensland 4811, Australia.

<sup>b</sup> Division of Science and Technology, Griffith University, Nathan, Queensland 4111, Australia.

The mediation of the electropolymerization of 4-methyl-4'-vinyl-2,2'-bipyridine (vbpy) by its coordination to transition metal centres is well established.<sup>1</sup>



The resultant films are immobilized on the electrode surface, and are found in general to maintain the homogeneous solution redox properties of the monomeric species: the films have therefore been the subject of much research into their use as electrocatalysts,<sup>1</sup> photoelectrocatalysts,<sup>1</sup> in electronic switching devices<sup>1</sup> and in the study of the mechanism of electron transfer.<sup>2</sup> In addition, in some cases the metal ion may be removed and subsequently replaced by an alternative metal ion.<sup>3</sup>

Despite the significant number of examples of the surface immobilization of metal complexes using vinyl derivatives of polypyridyl ligands, little is known about the mechanism of the polymerization process or of the size of the oligomer chain that deposits on the electrode surface.<sup>4</sup>

Work in our laboratories has developed a laser desorption/mass spectrometric technique which enables volatilization of large molecules, including polymers and metal complexes.<sup>5</sup> The present paper will report preliminary studies on the application of the laser desorption technique to the study of films polymerized onto glassy carbon electrode surfaces as a means of probing the nature of the polymer coatings.

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5. R. Beavis, J. Lindner, J. Grotemeyer, I.M. Atkinson, F.R. Keene, and A.E.W. Knight, *J. Am. Chem. Soc.* **1988**, *110*, 7534-7535; I.M. Atkinson, R.T.T. Karaiste, J.A. Shorter, F.R. Keene, and A.E.W. Knight, submitted for publication.



## LASER DESORPTION/TIME-OF-FLIGHT MASS SPECTROMETRY AND SPECTROSCOPY OF INVOLATILE COMPLEXES

R. Timo T. Karaiste,<sup>a</sup> Ian M. Atkinson,<sup>a</sup> Jeffrey A. Shorter,<sup>b</sup>  
Alan E. W. Knight,<sup>c</sup> and F. Richard Keene.<sup>a</sup>

<sup>a</sup> *Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Queensland 4811, Australia.*

<sup>b</sup> *NSF(USA)-DITAC(Australia) Exchange Scholar permanent address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.*

<sup>c</sup> *Division of Science and Technology, Griffith University, Nathan, Queensland 4111, Australia.*

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A number of techniques are available to introduce relatively involatile materials into a mass spectrometer, but the methods (such as fast-atom bombardment, FAB) often lead to substantial fragmentation of the molecular species involved. We have developed a composite silver-containing film matrix from which laser desorption, combined with laser ionization, minimizes fragmentation in both the vaporization and ionization processes. The matrixes are sufficiently temporally stable to enable the recording of wavelength scanned resonantly enhanced multiphoton ionization (REMPI) spectra of desorbed molecules.

In the present work, tris(bipyridine)ruthenium species have been laser desorbed from such matrixes without significant fragmentation. The desorbed molecules are entrained into a supersonic molecular beam of argon, and are thereby cooled rotationally and vibrationally (~5K and ~15K respectively). Tunable dye lasers are subsequently used to ionize the desorbed molecules in the source region of a time-of-flight mass spectrometer (TOF-MS).

The combination of laser desorption with TOF-MS detection and REMPI provides a means of recording the high resolution electronic spectra for a range of involatile complexes which have not hitherto been studied in the gas phase. A complex three-laser adaptation of this experiment has permitted to recording of the REMPI spectrum of  $[\text{Ru}(\text{bpy})_3]^{n+}$ .

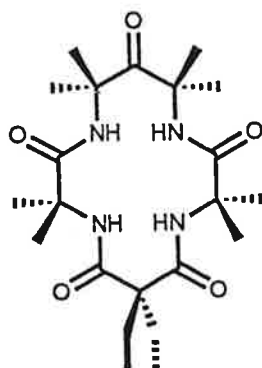
The paper will report on the detailed structure of the silver-containing matrix used in these experiments and possible mechanisms for laser desorption from them, and on the spectral studies on the desorbed species.

## NEW HIGH OXIDATION STATE IRON COMPLEXES

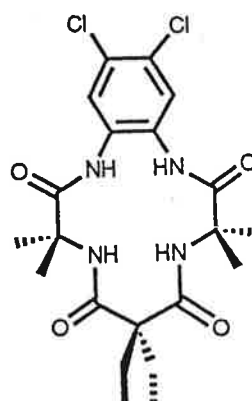
By Michael J. Bartos, Terrence J. Collins, Kimberly L. Kostka, Eckard Münck, Erich S. Uffelman, and L. James Wright<sup>†</sup>

*Contribution from the Departments of Chemistry, Carnegie Mellon University and The University of Auckland<sup>‡</sup>*

In its deprotonated form, the tetraamide macrocycle  $H_4[L_1]$ , is an excellent ligand for stabilizing metals in high oxidation states. Key features of this ligand are its resistance towards oxidation, the overall  $-4$  charge and the strong  $\sigma$ -donor properties of the amido nitrogen atoms. The iron(III) complex of this ligand,  $[NEt_4]_2[(L_1)Fe^{III}Cl]$ , can be easily prepared by reaction of  $H_4[L_1]$  with  $tBuLi$  and  $FeCl_2$  followed by air oxidation. Further oxidation of this complex by  $Ce(NH_4)_2(NO_3)_6$  in dichloromethane gives  $[NEt_4][(L_1)Fe^{IV}Cl]$ . The crystal structure of this complex has been obtained and the Mössbauer data at 150 K ( $\Delta E_Q = 0.87 \text{ mm s}^{-1}$ ,  $\delta_{Fe} = -0.03 \text{ mm s}^{-1}$ ) fully supports the iron(IV) oxidation state assignment. In a similar manner the deep purple compound,  $[NEt_4][(L_2)Fe^{IV}Cl]$ , has also been synthesized and studied.



$H_4[L_1]$



$H_4[L_2]$

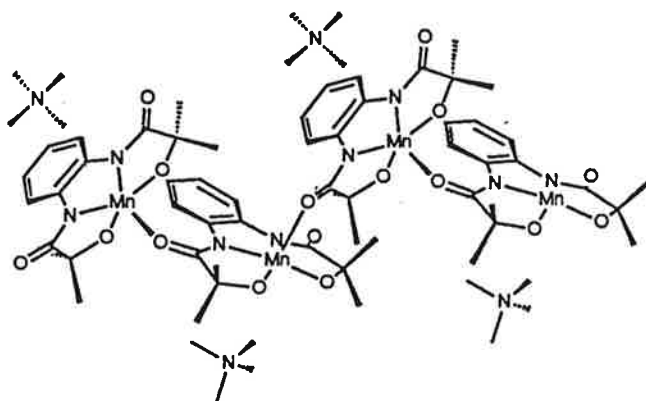
In contrast, if the oxidation of  $[NEt_4]_2[(L_2)Fe^{III}Cl]$  is carried out with  $tBuOOH$  in acetonitrile containing  $NEt_4OH$ , a deep blue solution is formed and a crystalline product of the same colour can be isolated by addition of excess  $PPh_4Cl$ . This product has been formulated as  $[PPh_4]_2[(L_2)Fe^{IV}-O-Fe^{IV}(L_2)]$  on the basis of Mössbauer, EPR, and IR spectroscopy, cyclic voltammetry and elemental analysis. Some chemistry of this compound and related derivatives, including the results of further oxidations, will be presented.

## A SPIN CHAIN OF $S = 2$ MANGANESE(III) CENTERS WITH NOVEL MAGNETIC PROPERTIES

By Terrence J. Collins, Edmund Day,<sup>†</sup> and Scott Gordon-Wylie

*Contribution from the Department of Chemistry, Carnegie Mellon University and the Department of Physics, Emory University<sup>†</sup>*

The quantum mechanics of spin chains have been dealt with by Haldane and the prediction is that chains of odd spins have a nondegenerate ground state, while chains of even spins have a degenerate ground state or perhaps two ground states separated by a small energy barrier. Large red-purple single crystals (1 x 4 x 10 mm) of the  $[(\text{CH}_3)_4\text{N}][\text{Mn}(\text{III})(\eta^4\text{-HMPA-B})]$  salt are revealed by x-ray crystallography to consist of parallel arrays of infinite chains of manganese atoms, much like spaghetti in a box (Figure). The Mn(III)'s are in a high spin  $S = 2$  configuration at room temperature. We have detected two magnetic states for this compound, one of high magnetic moment and one of low or zero magnetic moment. The transition energy barrier appears to be on the order of about 10k K in low applied fields of about 50 G.



The magnetic and structural properties of this novel compound will be presented. Changes in the magnetic properties on cooling are field dependent. In one extreme, if the temperature is lowered in applied fields  $> 1$  T, the spins become ferro- or ferrimagnetically ordered at a critical temperature of 3.7 K. In the other, if the temperature is lowered in small applied fields (50 – 200 G), then a state with a magnetic moment approaching zero results below 3.7 K. At zero applied field, the compound reproducibly exhibits spontaneous magnetization as the temperature crosses 3.7 K, indicating that the magnetic properties are 3-dimensional. These reproducible properties are observed in both powders and single crystals and we suspect that  $[(\text{CH}_3)_4\text{N}][\text{Mn}^{\text{III}}(\eta^4\text{-HMPA-B})]$  represents a type of ferromagnetic material that has not been previously encountered experimentally.

# ENERGETICS OF SOME ADDITION REACTIONS OF A TRINUCLEAR OSMIUM HYDRIDO COMPLEX

by Luigi Stradella

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via P. Giuria 9; 10125 - Torino , Italia

The reactions of osmium carbonyl clusters have been subjected to intense investigations as these complexes may play an important role in homogeneous catalysis (1).  $H_2Os_3(CO)_{10}$  is a well known hydride, which has been employed as starting material in several reactions to form osmium derivatives. At room temperature the 46-electron cluster  $(\mu-H)_2Os_3(CO)_{10}$  reacts with a Lewis base, L (L = phosphines, phosphites), to give the 48-electron saturated complex  $(\mu-H)(H)Os_3(CO)_{10}L$ .

Metal carbonyl reactions have been extensively studied by kinetics methods, but direct measurements of the reaction enthalpies are very uncommon. We report here some results concerning the adduct formation from osmium complexes. All measurements were performed at 300K with a Calvet microcalorimeter; the calorimetric cell we conceived to study reactions in the liquid phase have been already described (2).

The enthalpies of the reaction  $H_2Os_3(CO)_{10}$  "I" + L =  $H_2Os_3(CO)_{10}L$  "II" in chloroform are given in table 1.  $C^{13}$  NMR spectra of adduct "II" have shown that this reaction is quantitative (3).

Table I : Comparison between the electronic parameter ( $\nu$ ) and the enthalpy ( $\Delta H$ ) of the adduct formation

L	Electronic parameter $\nu$ , $cm^{-1}$	$\Delta H$ kcal/mol
$(i-Pr)_3P$	2059	107
$Et_2PPh$	2063	89
$Ph_2P$	2069	30
$(PhO)_3P$	2085	23

The decrease of the reaction heats is in qualitative agreement with basicity parameter,  $\nu$ , reflecting the donor ability of the phosphines and of the phosphite (4).

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- 4) A. Chadwick, Tolman, Chem. Rev., 77 (1977) 313

# ALKYNE COORDINATION, C≡C SCISSION AND ALKYNE DIMERIZATION ON TUNGSTEN-TRIIRIDIUM METAL CORES

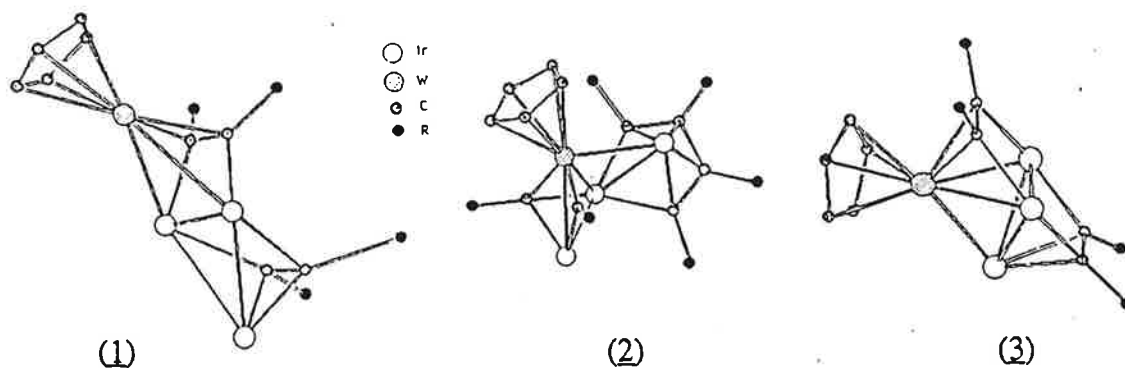
Mark G. Humphrey,<sup>1,2</sup> Colin H. McAteer,<sup>2</sup> Scott R. Wilson<sup>2</sup> and John R. Shapley<sup>2</sup>

1. Department of Chemistry, The University of New England, Armidale, NSW 2351, AUSTRALIA.
2. School of Chemical Sciences and Materials Research Laboratory, The University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA.

The reaction between the tetrahedral heteronuclear cluster  $\text{CpWIr}_3(\text{CO})_{11}$  and internal acetylenes has been examined and appears to proceed by two different pathways.

Hexafluorobut-2-yne reacted with the cluster under mild conditions to afford a mixture of (1;  $\text{R} = \text{CF}_3$ ), a butterfly cluster containing two ( $\sigma + 2\pi$ )-bound acetylene ligands, and (2;  $\text{R} = \text{CF}_3$ ), a butterfly cluster with both edge-bridging and face-capping phenylmethyldiylne ligands and an iridacyclopentadienyl iridium unit.

Reaction of  $\text{CpWIr}_3(\text{CO})_{11}$  with diphenylacetylene under more forcing conditions gave a mixture of (2;  $\text{R} = \text{Ph}$ ) and (3;  $\text{R} = \text{Ph}$ ), the latter a tetrahedral cluster with two ( $\sigma + 2\pi$ )-bound acetylene ligands. Complex (1;  $\text{R} = \text{CF}_3$ ) could be converted cleanly into (3;  $\text{R} = \text{CF}_3$ ) on heating. It proved impossible to interconvert (2) and (3), or to reform (1;  $\text{R} = \text{CF}_3$ ) by carbonylating (3;  $\text{R} = \text{CF}_3$ ). Complexes (1;  $\text{R} = \text{CF}_3$ ), (2;  $\text{R} = \text{Ph}$ ) and (3;  $\text{R} = \text{Ph}$ ) have been crystallographically characterized.



(carbonyl ligands have been omitted from all diagrams for clarity)

# CHAIN LENGTHENING AT CYCLOPENTADIENYLRUTHENIUM CENTRES BY INSERTION OF TERMINAL ACETYLENES INTO Ru-C(sp<sup>2</sup>) BONDS

Marie P. Cifuentes,\* Andrew Catlow, Michael R. Snow, Edward R.T. Tiekink and Michael I. Bruce

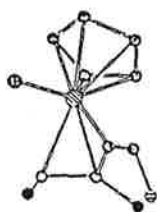
Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, SA 5001, AUSTRALIA

\* New address: Department of Chemistry, The University of New England, Armidale, NSW 2351, AUSTRALIA

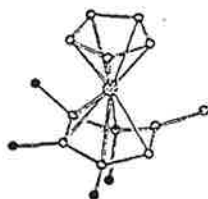
The reactions of terminal acetylenes with chelate vinyl ester and chelate butadienyl cyclopentadienylruthenium complexes have been investigated; both proceed by formal insertion of the acetylene into a Ru-C(sp<sup>2</sup>) bond, to afford derivatives containing  $\eta^3$ -allyl groups in the former case and cyclic  $\eta^5$ -ligands in the latter case.

Phenylacetylene reacted with  $\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{CHC}(\text{O})\text{OMe}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  to give the allylic derivative (1), rather than a butadienyl complex analogous to those isolated in earlier studies using internal acetylenes. In our current work, the intermediacy of a coordinated vinylidene explains the observed product.

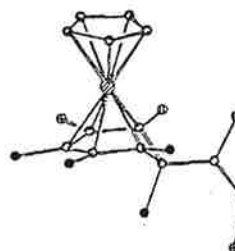
$\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  reacted with (tert-butyl)- and phenyl- acetylene to afford (2), which contains an  $\eta^5$ -cyclohexadienyl ligand. In the latter reaction, a small amount of the vinylcyclohexadienyl complex (3; R = Ph, R' = H) formed from addition of two acetylene molecules, was also isolated. The (R = R' = CO<sub>2</sub>Me) analogue was later structurally characterised. Preparative and structural details of these complexes will be presented, together with mechanistic speculation as to their formation.



(1)  $\bullet$  Ru  
 $\oplus$  P  
 $\circ$  C  
 $\text{Ph}$  Ph  
 $\bullet$  CO<sub>2</sub>Me



(2)  $\bullet$  Ru  
 $\bullet$  C  
 $\bullet$  CO<sub>2</sub>Me  
 $\circ$  Ph, t-Butyl



(3)  $\bullet$  Ru  
 $\circ$  C  
 $\bullet$  CO<sub>2</sub>Me  
 $\text{R} = \text{Ph}, \text{CO}_2\text{Me}$   
 $\text{R}' = \text{H}, \text{CO}_2\text{Me}$

## COBALT COMPLEXES AS HYPOXIA SELECTIVE ANTI-CANCER DRUGS.

David C. Ware, William A. Denny and William R. Wilson

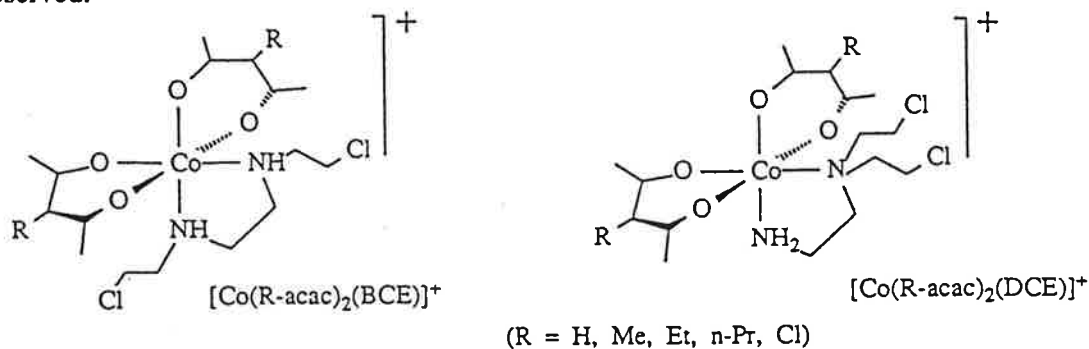
*Department of Chemistry, Cancer Research Laboratory, and Department of Pathology, The University of Auckland, Auckland, New Zealand.*

Targeting environmental differences, such as hypoxia, between tumors and normal tissues is a means of achieving selectivity in the rational design of anti-cancer drugs. We have been developing cobalt complexes as hypoxia-selective agents. Coordination of a small, cytotoxic molecule to an inert cobalt(III) center masks the cytotoxicity of the ligand. In an hypoxic environment, net chemical or metabolic reduction of the inert cobalt(III) complex to the very labile cobalt(II) species results in rapid aquation of the metal, releasing the now active cytotoxin and producing non-toxic  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . This mechanism can be viewed as a combined prodrug/selective drug delivery system.

We have identified and investigated a number of design criteria for suitable cobalt complexes. (i) The Co(III)/(II) reduction potential is in the range of cell reductants; (ii) the cytotoxic molecule must coordinate to the metal and in this form be rendered inactive; (iii) the small molecule must be released unchanged on reduction of Co(III) to Co(II); (iv) the reduced cobalt(II) complex must be sufficiently kinetically inert to ensure efficient reoxidation without ligand loss in oxygenated cells; and (v) the complex must be water soluble and stable under physiological conditions.

A ligand system which fulfils these criteria is based on the bis(2-chloroethyl)amine moiety, which is known to be a DNA interstrand cross-linking agent with potent cytotoxic activity. Two ligands containing this moiety, BCE and DCE, were incorporated into the two series of complexes  $[\text{Co}(\text{R-acac})_2(\text{BCE})]^+$  and  $[\text{Co}(\text{R-acac})_2(\text{DCE})]^+$  (as shown below). The synthesis and characterization of these complexes including  $^1\text{H}$  and  $^{13}\text{C}$  NMR, voltammetry and an X-ray crystal structure of  $[\text{Co}(\text{Cl-acac})_2(\text{BCE})]\text{ClO}_4$  will be detailed. Variation of the substituent R significantly affects the Co(III)/Co(II) reduction potential ( $E_{\text{pc}}$ ).

The cytotoxic potencies and hypoxic selectivities of these compounds were compared using growth inhibition of AA8 Chinese hamster fibroblasts. The cell cultures were exposed to the drugs under either aerobic or hypoxic conditions. Parallel experiments with UV4, a mutant selected from AA8 with a defect in the repair of DNA cross-links, were used to assess the mechanism of cytotoxicity. While cytotoxicity did not correlate with  $E_{\text{pc}}$ , the UV4 hypersensitivity factor ( $\text{HF} = \text{IC}_{50} \text{ AA8} / \text{IC}_{50} \text{ UV4}$ ) indicated that ligand release is the dominant mechanism of cytotoxicity for  $[\text{Co}(\text{R-acac})_2(\text{BCE})]^+$  ( $\text{R} = \text{H}, \text{Cl}$ ) and  $[\text{Co}(\text{R-acac})_2(\text{DCE})]^+$  ( $\text{R} = \text{H}, \text{Me}$ ). For two of these compounds significant hypoxia selective cytotoxicity was observed.



THE INTERACTION OF SOME LANTHANIDE IONS  
WITH HUMAN LACTOFERRIN

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Lactoferrin, along with the proteins serum transferrin and ovotransferrin, have the ability to bind tightly ( $K_{eq} \approx 10^{20}$ ) yet reversibly, 2  $Fe^{3+}$  ions concomitantly with 2 (bi)carbonate anions. In addition, it can also bind a wide variety of other metal ions, including most of the first row transition metals, the group 13 elements, the lanthanides and some of the actinides.

The binding of the lanthanides to the transferrins is interesting in a number of aspects. Firstly, in the case of transferrin, there is an apparent size selectivity: the larger ions, La-Nd have been reported to bind in a ratio less than the 2:1 expected<sup>1</sup>. Secondly, from the limited work that has been done on binding constants (Nd and Sm values only reported<sup>2</sup>), it appears that there is an increase in  $K_{eq}$  as the ionic radii decrease.

In this study, binding of a selected number of the lanthanide ions to lactoferrin was undertaken to investigate the extent and the relative strength of binding. Equilibrium binding constants for the second equivalent of metal ion were calculated from UV difference spectroscopy. No evidence for size selectivity was found. From the relative values of the binding constants it is clear that there is a trend to greater stability of the lanthanide-lactoferrin complexes with increasing atomic number. It also appears that the presence of traces of EDTA can interfere with binding.

Another interesting result of this work was the formation of a coloured lanthanide-lactoferrin complex: all the reported complexes to date have been colourless. Cerium added as  $Ce^{3+}$  initially produced no colour, but upon standing, an intense brown colour developed. We propose that oxidation of the  $Ce^{3+}$  to  $Ce^{4+}$  is taking place after binding, similar to that observed for cobalt and manganese<sup>3</sup>.

The implications of the binding of larger metal ions to lactoferrin will be discussed in terms of the known structure of the protein and the influences of the preferred coordination of the metal ions and the effect of nonsynergistic anions such as EDTA will also be considered.

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## X-RAY STRUCTURAL ANALYSIS OF REDUCED Cu(I) AZURIN FROM *ALCALIGENES DENITRIFICANS* AT 1.9Å RESOLUTION

By W Shepard<sup>\*</sup>, B F Anderson, E N Baker and G E Norris, Massey University,  
Palmerston North, New Zealand.

The crystal structure of the blue copper protein azurin from *Alcaligenes denitrificans* has been determined in its reduced Cu(I) state at pH 6.0. Azurin crystals were reduced by soaking in mother liquor containing 0.1M ascorbate for 7 hours. Diffractometer data was collected to 1.9Å resolution using a fast step scan routine. The oxidised azurin coordinates (J. Mol. Biol., 1988, 203, 1071-1095) provided a starting model for restrained least squares refinement (program PROLSQ). Following 134 cycles of refinement, interspersed with rebuilding of the model using a PS330 interactive graphics system and the graphics program FRODO, the final model contains 1966 protein atoms, 258 water molecules, and two sulphate anions. The final R-factor is 0.166.

The two azurin molecules in the asymmetric unit show good agreement (rms deviation 0.30Å for mainchain atoms). The most significant changes upon reduction occur at the copper, while the remainder of the molecule is left essentially unaltered. The whole copper coordination sphere is slightly expanded; copper to ligand distances and those to the axial groups (Met 121 and O 45) have increased by approximately 0.1Å. Both of these changes reflect a more Cu(I)-like geometry. The comparatively minor structural differences between the two redox forms of azurin are consistent with the requirements for fast electron transfer.

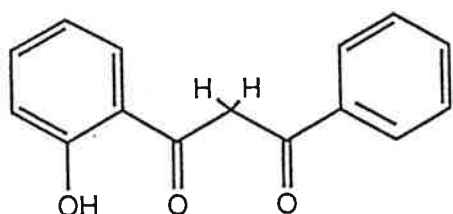
### Key-words

AZURIN  
COPPER PROTEIN  
PROTEIN CRYSTALLOGRAPHY

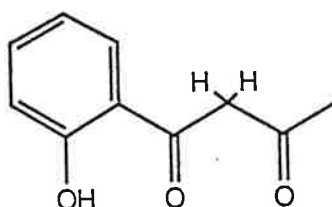
THE SYNTHESIS AND STRUCTURAL FEATURES OF URANYL (VI)  
COMPLEXES WITH 2-ACETOACETYLPHENOL AND  
2-BENZOYLACETOPHENOL.

R.J. Cresswell, E.W. Ainscough, A.M. Brodie and J.M. Waters  
Massey University Palmerston North, New Zealand.

The  $\beta$ -ketophenol ligands, 2-acetoacetylphenol ( $H_2aap$ ) and 2-benzoylacetylphenol ( $H_2bap$ ), can be utilised as binucleating ligands to prepare both homo- and hetero-binuclear complexes with the first row transition metals.<sup>1</sup>



$H_2bap$



$H_2aap$

In this work we have attempted to make the corresponding complexes with the uranyl ion ( $UO_2^{2+}$ ). When uranyl acetate and  $H_2aap$  or  $H_2bap$  are reacted in a 1:2 molar ratio in alcohol the mononuclear complexes  $[UO_2(Haap)_2EtOH]$  and  $[UO_2(Hbap)_2EtOH] \cdot EtOH$  are formed respectively.

However, the homo-binuclear complexes, e.g.  $[(UO_2)_2(aap)_2]$ , were not formed when a 1:1 molar ratio was used. Attempts to prepare heterobinuclear complexes by addition of the appropriate transition metal acetate to the mononuclear uranyl complexes have proved unsuccessful with the exception of manganese(II) acetate, which yielded  $[UO_2Mn(bap)_2] \cdot 1.5H_2O$ .

In an attempt to establish why such binuclear compounds are not easily isolated, we have performed single crystal x-ray structures on both the mononuclear compounds and structural arguments will be presented to account for the above observations.

Other spectroscopic features of these compounds will be discussed.

<sup>1</sup> Casellato, S; Tamburini, P.A.; Vigato, P.A.; De Stefani, A; Vidali, M; Fenton, D.A.  
*Inorg.Chim.Acta*, 69 (1983) 45-51.

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## MIXED-METAL AND MIXED-ANION DERIVATIVES OF HUMAN LACTOFERRIN

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**Musa S. Shongwe, Eric W. Ainscough, Heather M. Baker  
and Andrew M. Brodie.**

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

Structural analysis of human lactoferrin has provided definitive evidence for the presence of two ferric ions and two carbonate ions in the specific binding sites under physiological conditions. It has long been recognised that there must be concomitant binding of a synergistic anion to obtain a stable metal-lactoferrin complex. Over the past two decades, much attention has been paid to the replacement of carbonate in transferrin by other synergistic anions.

In our present work we have carried out a comparative study with lactoferrin by exploring the effects of various synergistic anions (including carbonate, malonate and oxalate) on the binding of transition metal ions to the protein. We have demonstrated that coordinating oxalate directly to a ferric ion in lactoferrin results in marked changes in the e.p.r. spectrum.

In addition, we have shown that in the presence of trace amounts of EDTA in the protein solution, one of the two specific binding sites cannot accommodate both iron and oxalate; instead, it binds iron and carbonate (if bicarbonate is supplied). The resulting mixed-anion, diferric lactoferrin complex appears to be stable in air and is reminiscent of the crystallographically determined dicupric analogue. Attempts to synthesise mixed-metal lactoferrin derivatives suggest that this area of protein chemistry might be fruitful.

## COPPER BINDING TO HUMAN LACTOFERRIN:

## A CRYSTALLOGRAPHIC STUDY

C. A. Smith, E. N. Baker and H. M. Baker

Department of Chemistry and Biochemistry, Massey University

Lactoferrin is a member of the family of iron-binding proteins known as the transferrins. They are all glycoproteins of molecular weight 80,000 Da, and are able to bind 2  $\text{Fe}^{3+}$  ions concomitantly with 2 (bi)carbonate anions. In addition, the transferrins also bind a variety of other metals such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{VO}^{2+}$ , the lanthanides and  $\text{Th}^{4+}$ . The synergistic anion requirements of the transferrins can be met with anions other than carbonate, including oxalate, malonate and thioglycolate.

The structures of iron-saturated human lactoferrin<sup>1</sup> and iron-saturated rabbit serum transferrin<sup>2</sup> both show a bilobal arrangement of the polypeptide chain, each lobe having one  $\text{Fe}^{3+}$  bound tightly in a cleft between two domains. The structure of metal-free lactoferrin has also been solved and in this molecule, the N-lobe is wide open, with no metal bound, while the C-lobe remains tightly closed with no bound iron<sup>3</sup>, as in the diferric form.

These structures clearly demonstrate the existence of conformational flexibility in the protein and raise a number of questions related to metal and anion binding. The first is whether closure of the domains over varies according to the size, charge and coordination preferences of the metal or anion. The selectivity in anion binding between the two sites in both lactoferrin<sup>4</sup> and transferrin<sup>5</sup>, where, in the presence of copper, only one oxalate binds, along with the lack of selectivity in ovotransferrin, where two oxalate bind<sup>6</sup>, poses other questions related to differences between the proteins and to differences between the two binding sites.

To obtain structural information on metal and anion binding to lactoferrin, both dicupric lactoferrin and a complex containing 2  $\text{Cu}^{2+}$ , one oxalate and one carbonate were prepared and crystallised. X-ray data to 2.1 Å have been collected from both and the structures solved. Some of the important structural features will be reported and discussed in this poster.

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## CADMIUM BINDING BY AZURIN

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Department of Chemistry and Biochemistry  
Massey University

Azurin is one of the blue copper electron transfer proteins. The structures of its oxidised (1), reduced (2) and apo-states have been determined by X-ray crystallography. These suggest that the copper site is determined by the constraints of the protein structure, and that it alters little during redox changes, or on the removal of the copper.

Experiments on the binding of cadmium have been carried out, to test this idea and to investigate the effects of binding another metal. This work is also relevant to  $^{113}\text{Cd}$  NMR studies (3), which show similar spectra for azurin and stellacyanin, but differences for plastocyanin.

Crystals of Cd-azurin were prepared by removing copper from crystals of Cu-azurin and soaking these in  $\text{Cd}(\text{NO}_3)_2$  solution. X-ray data to  $2.3\text{\AA}$  have been collected and preliminary refinement carried out. ( $R = 18.0\%$  for a model comprising 1956 protein atoms and 39 water molecules). The metal site is only partially occupied by cadmium (occupancy  $\approx 40\%$ ), but reveals interesting differences in coordination. In particular, a nearby carbonyl oxygen has moved closer, to give a stronger interaction with cadmium than with copper ( $\text{Cd-O} = 2.6\text{\AA}$  compared with  $\text{Cu-O} = 3.1\text{\AA}$ ).

Coupled with the  $^{113}\text{Cd}$ -NMR data, these results are consistent with the idea that there may be an oxygen-metal interaction in the binding site of stellacyanin.

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## STRUCTURAL, SPECTROSCOPIC AND PHOTOCHEMICAL STUDIES ON PHENYLTHIOUREA TRIOSMIUM CLUSTER COMPOUNDS

S.L.Ingham, E.W.Ainscough, A.M.Brodie and J.M.Waters, Massey University, Palmerston North, New Zealand.

In recent years there has been considerable interest in the chemistry of osmium clusters<sup>1,2</sup>. They are good model compounds for adsorbates on a metallic surface in a heterogeneous catalytic system and some are potential homogeneous catalysts for reactions of industrial importance. With clusters larger than trinuclear most interest has been in their skeletal shapes and how these are determined by the outer coordination shell or encapsulated atoms. However triosmium clusters are generally easily handled in air, are easily crystallised and usually easy to characterise.

The reaction of decacarbonylbis(acetonitrile)triosmium with phenylthiourea, or diphenylthiourea proceeds smoothly in dichloromethane to give the  $\mu$ -hydrido,  $\mu$ -thioureato decacarbonyltriosmium cluster. Reactions of these clusters with 1 mole of trimethylamine N-oxide, or photolysis in cyclohexane, removes 1 mole of carbon monoxide to yield the nonacarbonyltriosmium cluster where the thioureato ligand serves as a triple bridge with the sulphur bound to two osmium atoms and a nitrogen bound to the third. Structural, spectroscopic and photochemical data will be presented on these compounds.

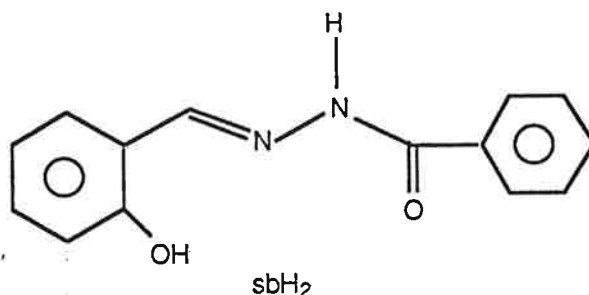
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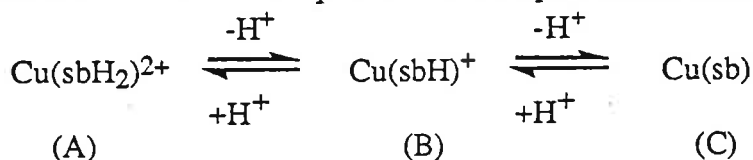
# ANTITUMOUR COPPER COMPLEXES - STRUCTURAL STUDIES OF NEUTRAL AND DEPROTONATED SALICYLADEHYDE BENZOYLHYDRAZONE COMPLEXES

A.J. Dobbs, E. W. Ainscough, A. M. Brodie, J. R. Ranford and J. M. Waters.  
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Massey University  
Palmerston North  
New Zealand

It is known that even though salicylaldehyde benzoylhydrazone (sbH<sub>2</sub>) inhibits DNA synthesis, the copper complexes of this tridentate ONO hydrazone showed up to a 100 - fold increase in potency. We have extended these studies to a range of variously substituted sbH<sub>2</sub> derivatives and their cytotoxicity against HCT-8 cells evaluated.



Here we report on some extended synthetic studies of the copper(II)/sbH<sub>2</sub> system and show that the nature of the complex formed is dependent on the conditions employed.



Three different types of complexes can be isolated (compounds A, B and C). A single crystal X-ray structure of [Cu(sbH<sub>2</sub>)(CCl<sub>3</sub>COO)<sub>2</sub>]<sub>2</sub> which is representative of an (A) type, is a centrosymmetric dimer with the copper(II) centres bridged by the protonated phenoxy oxygens on the sbH<sub>2</sub> ligands. The complex [{Cu(sbH)(H<sub>2</sub>O)}<sub>2</sub>SiF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O which is representative of a (B) type, is also a centrosymmetric dimer with the copper(II) centres bridged by the SiF<sub>6</sub><sup>2-</sup> moiety. Further structural details of each and a comparison of the two (especially as far as the hydrazone ligands are concerned) will be given, along with that for [Cu(sbH)Cl]·H<sub>2</sub>O whose structure has already been determined [1].

The relevance of this work to an antitumour mechanism will be briefly discussed.

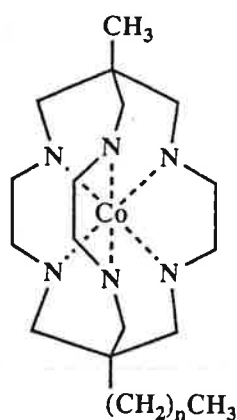
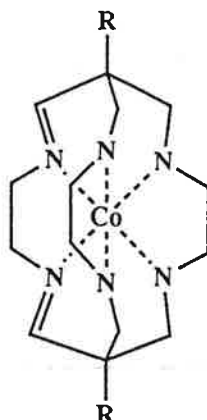
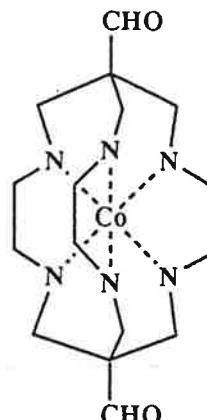
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## A New and Efficient Strategy for Synthesising Cage Complexes

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It is now 13 years since the synthesis of  $[\text{Co}(\text{sepulchrates})]^{3+}$  from tris(ethylenediamine) cobalt(III), ammonia and formaldehyde was first reported.<sup>(1)</sup> Since that time many derivatives of sepulchrates and sarcophagine type cage complexes have been synthesised,<sup>(2)</sup> virtually all based on reactions with metal templates in aqueous solution<sup>(3)</sup> and mostly with formaldehyde and nitromethane as the capping reagents.

Recently, another efficient route to both new and existing cage molecules via a  $[\text{Metal}(\text{en})_3]^{n+}$  template in acetonitrile has been developed. The method is akin to the Curtis macrocycle synthesis<sup>(4)</sup> but employs new capping strategies and provides ways to synthesise previously inaccessible compounds. The process also gives a more generalised approach to many different types of functionalised cage complexes either through reaction at an apical carbanion intermediate, or by modification of apical formyl functions.

(1)  $n = 0 \text{ to } 11$ (2)  $R = \text{CH}_3, \text{H}$ 

(3)

The synthetic procedure and some of the wide range of new compounds accessible by this technique will be reported.

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# Electron Transfer in Encapsulated Metal Ion Systems: A Confirmation of the Marcus-Hush Theory

I.I. Creaser, <sup>a</sup> P. Bernhard, <sup>a</sup> E. Miles, <sup>a</sup> A.M. Sargeson, <sup>a</sup> G.W. Walker <sup>a</sup> and A.W. Zanella<sup>b</sup>

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b. Joint Science Department, Claremont Colleges, Claremont, California, 91711, U.S.A.

The properties of encapsulated metal ions provides a system which is uniquely suited to the study of outer sphere electron transfer phenomena.<sup>(1)</sup> The inertness of the complexes for many metal ions in a range of oxidation states and the ability to measure electron self exchange rates accurately ensure outer sphere electron transfer and offer an opportunity to rigorously test the Marcus-Hush theories <sup>(2)</sup> over a range of metal ions.

We have determined the cross reaction rate constants for electron transfer between many cage complexes of Fe, Mn, Ru, Ni and Co. A high degree of correlation between the experimentally observed rate constant and that predicted by the Marcus-Hush theory was obtained. This correlation was obtained over the full range of orbital symmetries and appropriate examples are shown below.

Reaction	Orbital Symmetry	$k_{\text{obs}}, \text{M}^{-1}\text{s}^{-1}$	$k_{\text{calc}}, \text{M}^{-1}\text{s}^{-1}$
$\text{Co}(\text{diCl sar})^{2+} + \text{Fe}(\text{sar})^{3+}$	$e_g \rightarrow t_{2g}$	$5.3 \times 10^4$	$9.6 \times 10^4$
$\text{Ru}(\text{sar})^{2+} + \text{Mn}(\text{sar})^{3+}$	$t_{2g} \rightarrow e_g$	$1.7 \times 10^5$	$0.9 \times 10^5$
$\text{Mn}(\text{sar})^{2+} + \text{Ni}(\text{sar})^{3+}$	$e_g \rightarrow e_g$	$1.0 \times 10^5$	$0.7 \times 10^5$
$\text{Ru}(\text{sar})^{2+} + \text{Ru}(\text{tacn})^{3+}$	$t_{2g} \rightarrow t_{2g}$	$7.3 \times 10^5$	$3.4 \times 10^5$

The results of a range of such experiments will be presented and the implications discussed.

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## RUTHENIUM AND OSMIUM-SILYL COMPLEXES

G.R. Clark, C.E.F. Rickard, W.R. Roper, D.M. Salter, and L.J. Wright

Department of Chemistry, University of Auckland, Auckland

Recent advances in transition metal-silicon chemistry have yielded both base-stabilised and base-free transition metal-silylene complexes.<sup>1</sup> Our research involves the generation of new ruthenium- and osmium-silyl complexes, as precursors that may lead to transition metal-silylene species. Complexes having a coordinatively unsaturated environment are of particular interest.

Reaction of  $MPhCl(CO)(PPh_3)_2$  ( $M = Ru, Os$ ) with various silanes, as well as  $MHCl(CO)(PPh_3)_3$  with  $HSiCl_3$  or  $HSiMe_2Cl$ , results in the formation of  $M(SiR_3)Cl(CO)(PPh_3)_2$ . Further reactions can be carried out on the silicon group without disrupting the silicon-metal bond. For the bound  $SiCl_3$  and  $SiMe_2Cl$  groups, reactions have been attempted with O, N and S-centred nucleophiles and with carbanions to give derivatives such as  $Ru[Si(OEt)_3]Cl(CO)(PPh_3)_2$  and  $Os(SiMe_3)Cl(CO)(PPh_3)_2$ .

Several crystal structures have been performed. A typical example,  $Ru(SiEt_3)Cl(CO)(PPh_3)_2$ , shows a distorted square pyramidal geometry with the silicon ligand in the apical position.

Reaction of zero-valent  $Os(CO)_2(PPh_3)_3$  with  $HSiR_3$  results in oxidative addition of the silane to yield  $Os(SiR_3)H(CO)_2(PPh_3)_2$  complexes.

1. Straus, D.A.; Grumbine, S.D.; Tilley, T.D. *J.Am.Chem.Soc.*, **1990**, *112*, 7801.

BORON COMPLEXES OF TETRA-*p*-TOLYLPORPHYRINWarwick J Belcher and Penelope J Brothers

Department of Chemistry, University of Auckland

The coordination of boron to a porphyrin macrocycle using  $\text{BCL}_3 \cdot \text{MeCN}$  adduct as metal carrier was reported in 1977<sup>1</sup>. The initially obtained chloro-boron porphyrin complex was completely hydrolysed on chromatography to give a product formulated as a tetrahydroxydiboron porphyrin. However, the complexes obtained were never unambiguously characterised and no subsequent work in this area has been reported.

We have reinvestigated this chemistry with the aim of characterising the boron porphyrin products. In addition, the chemistry has been extended to include derivatised boron metal carriers such as  $\text{BPhCl}_2$ . Unlike the other members of Group 13 the small ionic radius of boron (III) ( $0.23 \text{ \AA}$ ) results in coordination of two boron atoms to the porphyrin in an "out of plane" geometry. The complexes formed are very labile, demetalating readily in protic solvents. The reactions of these complexes with alcohols and other nucleophiles have been investigated and have produced new aryloxo- and alkoxo- substituted boron porphyrin complexes.

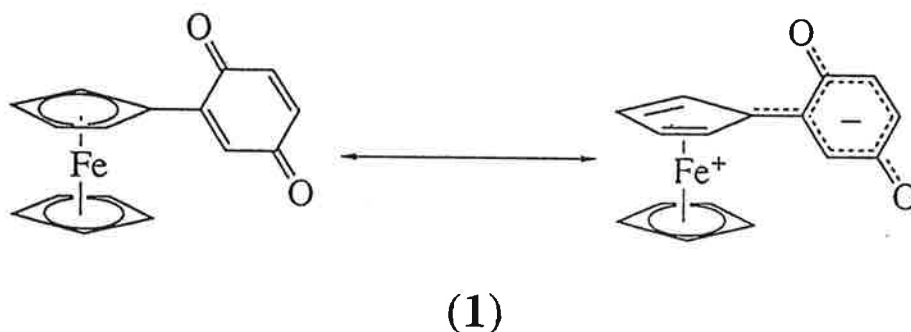
1. C.J. Carrano and M. Tsutsui, J.Coord.Chem., 1977, **7**, 125

# SYNTHESES AND ELECTRON TRANSFER PROPERTIES OF *para*-BENZOQUINONYL SUBSTITUTED FERROCENES.

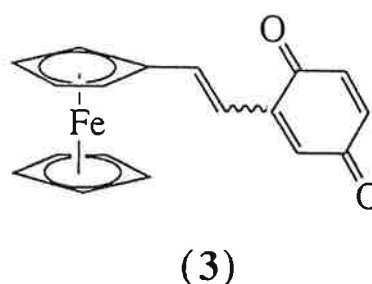
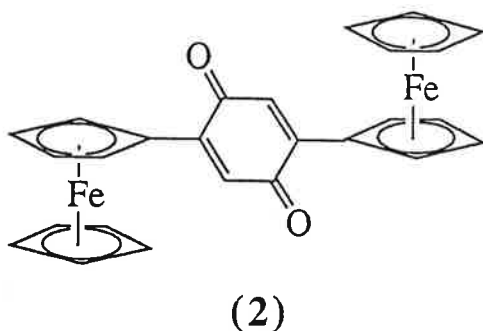
Katherine A. Walker and Stephen B. Colbran.

*Department of Inorganic and Nuclear Chemistry, The University of  
New South Wales, Sydney, NSW 2033, AUSTRALIA.*

The ferrocenylbenzoquinone (1)<sup>1</sup> has been prepared from 1-ferrocenyl-2,5-dimethoxybenzene by cleavage of the methoxy groups followed by oxidation of the resulting ferrocenylhydroquinone. Investigations using cyclic voltammetry, and infrared, uv-visible and Mössbauer spectroscopies reveal that (1) undergoes pH dependent intramolecular charge transfer from the iron atom to the quinonyl group as well as pH dependent intermolecular electron transfer. These results will be presented along with the characterisation of (1<sup>+</sup>•), (1<sup>-</sup>•), and (1.H<sup>+</sup>).



Extension of the preparative methodology used for (1) to the syntheses of ferrocenylquinones (2), (3) will also be described.



1. A. Kasahara *et al*, *Yamagata Daigaku Kiyo Kogaku*, 1985, 18, 125.

# SYNTHESIS AND REACTIONS OF $\sigma$ -METHYL $\beta$ -DIK COMPLEXES OF Pd(II) AND Pt(II)

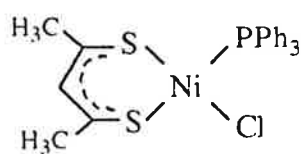
Hong Jin and Kingsley J. Cavell

*Department of Chemistry, University of Tasmania, Hobart Tasmania 7001*

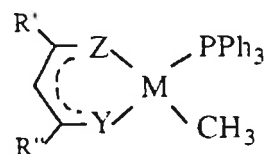
Homogeneous catalyst systems based on the nickel complexes(I) have proved to be extremely active and versatile catalysts for olefin oligomerization and for double-bond shift isomerization. The nature of the active species and the manner in which the ligands modify the insertion and elimination step in the proposed oligomerization mechanism is unknown. Hence the preparation of new Pd(II), Pt(II) model compounds is a major goal to understand the mechanism of this catalytic cycle.

Sodium  $\beta$ -diketonates and sodium mono-thio- $\beta$ -diketonates readily react with  $\text{PtMe(THF)}_x(\text{PPh}_3)_2$ , which is generated in situ from *trans*- $\text{PtMeI(PPh}_3)_2$  and  $\text{TiPF}_6$  in THF at room temperature, to yield a various of new O,O'-chelated, or O, S-chelated,  $\beta$ -dik complexes  $\text{PtMe}(\beta\text{-dik})(\text{PPh}_3)$ (1-4). The palladium(II) analogues  $\text{PdMe}(\beta\text{-dik})(\text{PPh}_3)$ (5-8) have been prepared similarly from *trans*- $\text{PdMeI(PPh}_3)_2$ .

In reaction with CO, most of these complexes give the corresponding metal acyl complexes  $\text{MC(O)Me}(\beta\text{-dik})(\text{PPh}_3)$ (9). The ease of the CO insertion reaction varies with the metal atom and with different  $\beta$ -dik ligands. The reactions of these complexes with acetylenes and olefins have also been investigated.



I



M=Pt or (Pd)

1(5): R' = R'' = Me, Z = Y = O;

2(6): R', R'' = Me or CF<sub>3</sub>, Z = Y = O;

3(7): R' = R'' = Me, Z = O, Y = S;

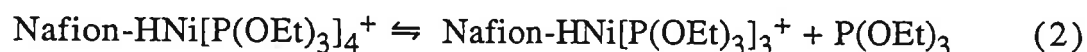
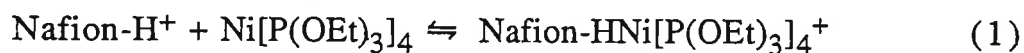
4(8): R' = Ph, R'' = Me, Z = O, Y = S

## A UNIQUE APPLICATION OF ACID-NAFION AS A CO-CATALYST AND SUPPORT.

Andrew J. Seen and Kingsley J. Cavell,

*Chemistry Department, University of Tasmania, Australia.*

The perfluorinated ion-exchange polymer, Nafion-H<sup>+</sup>, has been used as a Bronsted acid to activate Ni[P(OEt)<sub>3</sub>]<sub>4</sub> and as a support for the resulting cationic species.



Spectroscopic evidence has confirmed that the species present within the Nafion-H<sup>+</sup> film are the same as those found in a homogeneous solution using H<sub>2</sub>SO<sub>4</sub> as the Bronsted acid.

Isomerization of 1-octene using the supported system displayed linear activity for 60 to 180 minutes, the period of time being approximately inversely proportional to the amount of Nafion-H<sup>+</sup> present. Activity over the first 30 minutes was at best about a third of the activity obtained using H<sub>2</sub>SO<sub>4</sub> as co-catalyst, and varied linearly with the amount of Nafion-H<sup>+</sup> present. Comparative tests with 1-butene employing homogeneous and supported catalyst systems have found a relative doubling in isomerization rate on changing from 1-octene to 1-butene when using the supported system. This indicates that diffusion of 1-octene into, and products out of, Nafion-H<sup>+</sup> are controlling factors.

It has also been demonstrated that very little, if any, of the catalyst species is leached from the support.

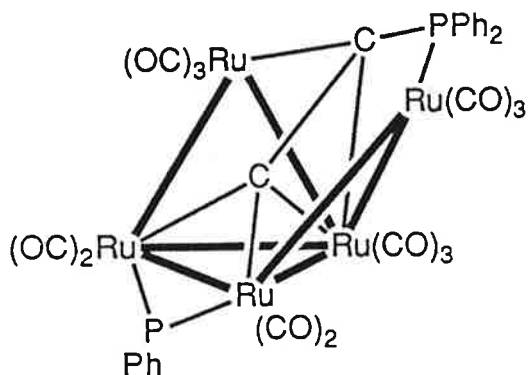
REACTIONS OF AN OPEN Ru<sub>5</sub> CLUSTER

Chris J. Adams<sup>1</sup>, Michael I. Bruce<sup>1</sup>, Brian W Skelton<sup>2</sup> and Allan H. White<sup>2</sup>

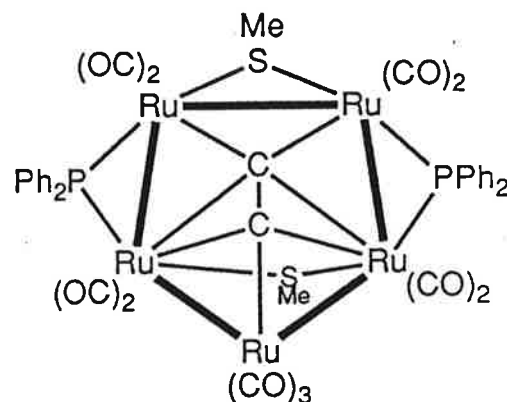
- 1 *Jordan Laboratories, Department of Physical and Inorganic Chemistry University of Adelaide, Adelaide, South Australia 5001 (Australia).*  
 2 *Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009 (Australia).*

Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(CO)<sub>13</sub> (I) contains an open Ru<sub>5</sub> cluster interacting with a diphenylphosphinoethynyl group. Reaction with a variety of reagents results in cleavage of the C-P bond to give a cluster-bound C<sub>2</sub> unit.

The reaction of (I) with Me<sub>2</sub>S<sub>2</sub> produces Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(μ-SMe)<sub>2</sub>(CO)<sub>13</sub>, which on heating is converted to Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>)(μ-PPh<sub>2</sub>)<sub>2</sub>(μ-SMe)<sub>2</sub>(CO)<sub>12</sub>, followed by Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>)(μ-PPh<sub>2</sub>)<sub>2</sub>(μ-SMe)<sub>2</sub>(CO)<sub>11</sub> (II). (II) contains a Ru<sub>5</sub> pentagon interacting with a C<sub>2</sub> unit.



(I)



(II)

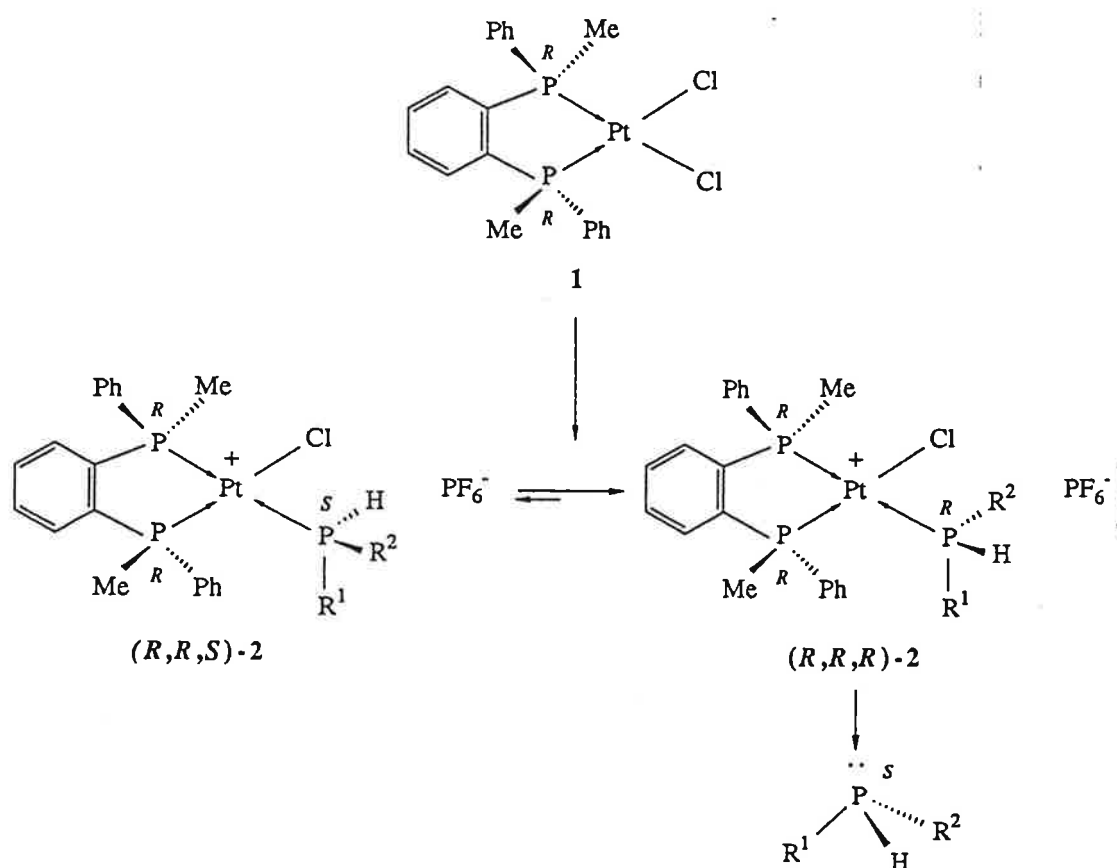
Reactivity of the C<sub>2</sub> unit in (II) is illustrated by its reaction with H<sub>2</sub>, ethene and phenylacetylene to produce Ru<sub>5</sub>(μ<sub>5</sub>-CCH<sub>2</sub>)(μ-PPh<sub>2</sub>)<sub>2</sub>(μ<sub>3</sub>-SMe)<sub>2</sub>(CO)<sub>10</sub>, Ru<sub>5</sub>(μ<sub>5</sub>-CCHCHCH<sub>2</sub>)(μ-PPh<sub>2</sub>)<sub>2</sub>(μ<sub>3</sub>-SMe)<sub>2</sub>(CO)<sub>10</sub> and Ru<sub>5</sub>(μ<sub>5</sub>-CCCHCPh)(μ-PPh<sub>2</sub>)<sub>2</sub>(μ-SMe)<sub>2</sub>(CO)<sub>10</sub> respectively.

# RESOLUTION OF SECONDARY PHOSPHINES BY METAL COMPLEXATION

A. Bader, G. Salem, and S.B. Wild

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

Chloride abstraction from optically active  $(R,R)$ -[PtCl<sub>2</sub>(diph)] {1, diph = 1,2-phenylenebis(methylphenylphosphine)}, followed by treatment of the solvated intermediate with secondary phosphines of the type  $(\pm)$ -PHR<sup>1</sup>R<sup>2</sup> and NH<sub>4</sub>PF<sub>6</sub>, affords the cationic complexes  $(R,R,S)$ - and  $(R,R,R)$ -[PtCl(diph)(PHR<sup>1</sup>R<sup>2</sup>)]PF<sub>6</sub> (2). The diastereomer  $(R,R,R)$ -[PtCl(diph)(PHMePh)]PF<sub>6</sub> has been isolated by fractional crystallization. Liberation of  $(S)$ -PHR<sup>1</sup>R<sup>2</sup> from complexes of type 2 by displacement with other ligands provides an effective route to the first optically resolved secondary phosphines.

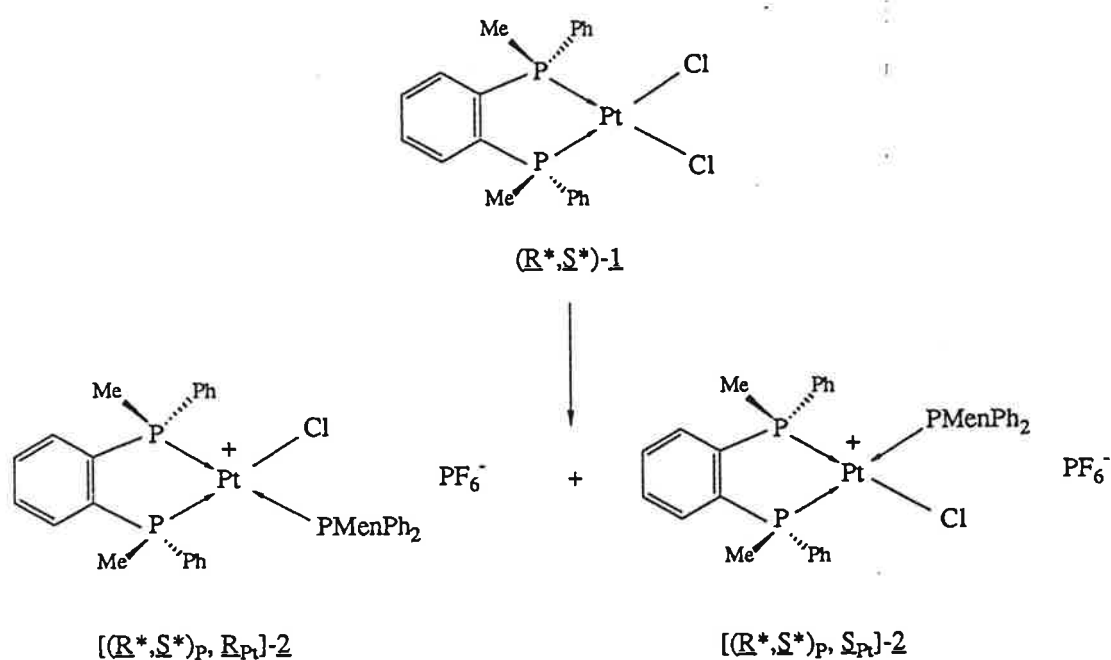




## RESOLUTION OF CHIRAL PLATINUM COMPLEXES

S. Limmer, G. Salem, and S.B. Wild*Research School of Chemistry, Australian National University,  
Canberra, A.C.T. 2601, Australia*

The complex  $(R^*,S^*)\text{-[PtCl}_2(\text{diph})]$ ,  $(R^*,S^*)\text{-1}$ , reacts with one equivalent of silver nitrate in acetone to produce a solvated intermediate, which, when treated with  $(-)$ -menthyldiphenylphosphine and ammonium hexafluorophosphate affords a 1:1 diastereomeric mixture of the salts **2**, chiral at platinum. The mixture can be separated by fractional crystallisation from boiling methanol. Related work with other meso ligands will be presented, as well as our results concerning the stability and stereoselectivity of substitution of the chloride ion in the pure diastereomers of **2**.

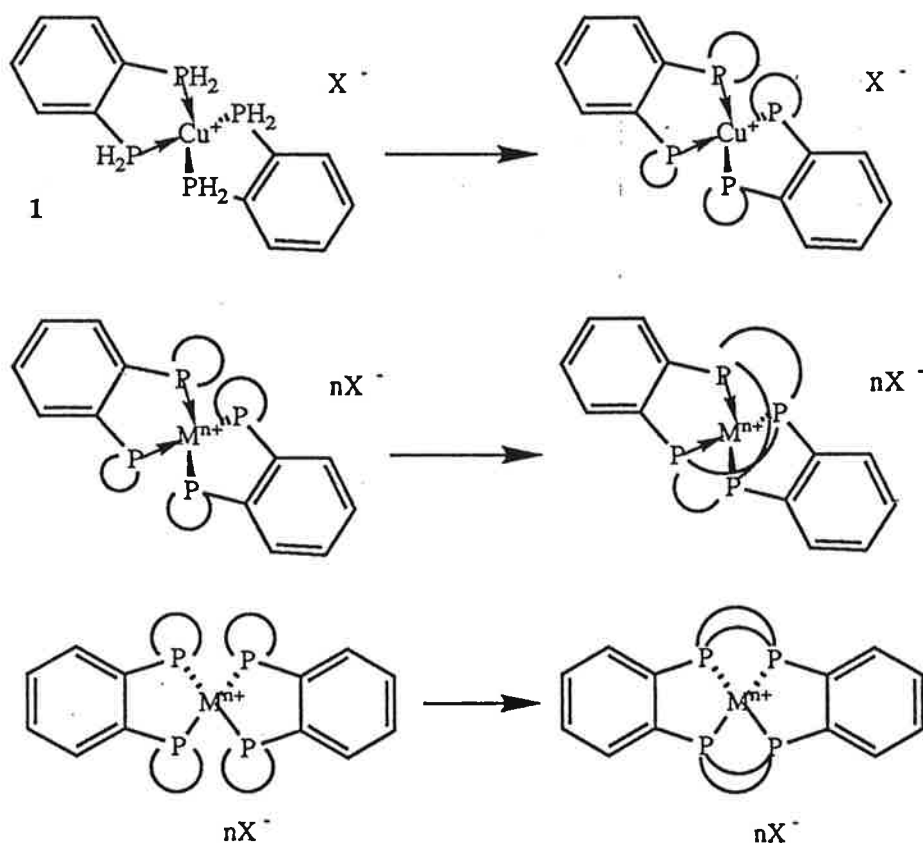


# TEMPLATE SYNTHESSES OF PHOSPHORUS MACROCYCLES AND CAGES

Y.B. Kang, D.D. Pathak, and S.B. Wild

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

The reaction of  $[\text{Cu}\{1,2\text{-C}_6\text{H}_4(\text{PH}_2)_2\}_2]\text{CF}_3\text{SO}_3, \mathbf{1}$  ( $\text{X} = \text{CF}_3\text{SO}_3$ ) with 4 equiv. of the dibromo alkanes  $\text{Br}(\text{CH}_2)_n\text{Br}$  (where  $n = 3 - 5$ ) in the presence of base affords cyclic bis(tertiary phosphine) complexes, from which the respective cyclic bis(tertiary phosphines) can be displaced in high yield. The conversion of the cyclic bis(tertiary phosphines) into the chelating diastereomers of tetra(tertiary phosphine) macrocycles and cages is being investigated as indicated. Related work on the chemistry of 3- and 4-membered rings containing phosphorus and arsenic will also be presented.



**COMPLEXES OF GROUP 11 METAL HALIDES WITH PHOSPHORUS DONOR LIGANDS. INVESTIGATIONS OF STRUCTURE AND BONDING BY X-RAY CRYSTALLOGRAPHY, INFRARED SPECTROSCOPY, AND CP/MAS  $^{31}\text{P}$  NMR SPECTROSCOPY**

Graham A. Bowmaker and Lisa-Jane Baker (University of Auckland), Saeed Attar and John H. Nelson (University of Nevada), Peter C. Healy (Griffith University), and Allan H. White (University of Western Australia)

**Abstract**

The Group 11 metals in the +I oxidation state ( $\text{Cu}^{\text{I}}$ ,  $\text{Ag}^{\text{I}}$  and  $\text{Au}^{\text{I}}$ ) display a wide diversity in their structural chemistry, and this is well illustrated by the variety of structural types which are encountered in complexes of copper(I) halides. Neutral phosphine and amine ligands form mononuclear or multinuclear complexes with copper (I) halides in which the copper coordination number ranges from 2 to 4. The greatest range of structural types has been found for the case of tertiary phosphine ligands, of which the most extensively studied is triphenylphosphine,  $\text{Ph}_3\text{P}$ .

In the present work, the study of these types of complexes has been extended to other phosphorus donor ligands which are closely related to  $\text{PPh}_3$ . With the highly basic and sterically hindered ligand tris(2,4,6-trimethoxyphenyl)phosphine, it has been possible to prepare for the first time a valence isoelectronic series of two-coordinate complexes of the type  $\text{LMX}_2$  ( $\text{M}=\text{Cu}, \text{Ag}, \text{Au}$ ), and the structural and spectroscopic characterization of these species will be given.

With the phosphole ligands 1-phenyl-3,4-dimethylphosphole (DMPP) and 1-phenyl-dibenzophosphole (DBP), complexes of the type  $[\text{L}_n\text{MX}]_m$  ( $\text{M}=\text{Cu}, \text{Ag}$ ) have been prepared and characterized. This study demonstrates the power of the combined use of far-infrared and solid state CP/MAS  $^{31}\text{P}$  NMR spectroscopy for obtaining structural information for these types of compound.

In both of the above studies, new ionic structures of the type  $[\text{L}_n\text{M}]^+[\text{MX}_2]^-$ , have been observed in the solid state.

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**Coordinated acetylene dianions: *Acetyleno* complexes of W(VI), W(V) and W(IV)**

P.D.W. Boyd, G.R.Clark, J.B.Metson, A.J.Nielson, C.E.F.Rickard and P.Schwerdtfeger.  
(Department of Chemistry, University of Auckland)

Reduction of  $[W(PhC_2Ph)Cl_4]$  with sodium-mercury amalgam in the presence of phosphines ( $P = PMe_3, PMe_2Ph, PMePh_2$ ) yields the complexes  $[W(PhC_2Ph)Cl_3(P)_2]$  which on the basis of magnetic susceptibility measurements, esr and XPS spectra are  $d^1$  systems containing the *acetyleno* ligand  $PhC=CPh^2$ . Further reduction gives the complexes  $[W(PhC_2Ph)Cl_2(P)_3]$ , ( $P = PMe_3, PMe_2Ph$ ) characterised as  $d^2$  *acetyleno* complexes. Crystal structures of the  $d^1$  and  $d^2$  phosphine complexes have been carried out. Theoretical studies (ab initio molecular orbital and scattered wave  $X\alpha$  calculations) support the existence of acetylene dianions in the model  $d^0$  and  $d^1$  species  $[W(HC=CH)Cl_3]^-$  and  $[W(HC=CH)Cl_3(PH_3)_2]$ .

COORDINATIVELY UNSATURATED  $\sigma$ -ARYL  
COMPLEXES OF IRIDIUM (III)

W R ROPER and G C SAUNDERS

Department of Chemistry, University of Auckland,  
Auckland

Analogously to the reactions between  $\text{MHCl}(\text{PPh}_3)_3(\text{CO})$  ( $\text{M} = \text{Ru}, \text{Os}$ ) and  $\text{HgR}_2$  ( $\text{R} = \text{phenyl}, p\text{-tolyl}, o\text{-tolyl}$ ), which proceed with loss of mercury to yield  $\text{MRCl}(\text{PPh}_3)_2(\text{CO})$ ,  $\text{IrHCl}_2(\text{PPh}_3)_3$  reacts with  $\text{HgR}_2$  ( $\text{R} = \text{phenyl}, p\text{-tolyl}$ ) to yield the dichroic five coordinate iridium (III) complexes  $\text{IrRCl}_2(\text{PPh}_3)_2$ . In contrast  $\text{IrHCl}_2(\text{PPh}_3)_3$  reacts with  $\text{Hg}(o\text{-tolyl})_2$ , retaining mercury, to yield the red five coordinate iridium (III) complex  $\text{Ir}(o\text{-tolyl})\{\text{Hg}(o\text{-tolyl})\}\text{Cl}(\text{PPh}_3)_2$ , which contains an iridium-mercury bond as evidenced by the  $^{31}\text{P}$  n.m.r. spectrum, which gives a value of  $J(\text{P}-^{199}\text{Hg})$  of 204.5 Hz. The structure of  $\text{Ir}(o\text{-tolyl})\{\text{Hg}(o\text{-tolyl})\}\text{Cl}(\text{PPh}_3)_2$ , which may adopt square pyramidal geometry, as for  $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{PPh}_3)_2(\text{CO})$ , or trigonal bipyramidal geometry, as for  $\text{Ru}(o\text{-tolyl})\text{Cl}(\text{PPh}_3)_2(\text{CO})$ , is of interest in view of recent theoretical calculations. These coordinatively unsaturated iridium (III) complexes coordinate two electron donor ligands, such as CO and  $p\text{-tolylNC}$ , to give pale yellow or white six coordinate complexes. The complex  $\text{Ir}(o\text{-tolyl})\{\text{Hg}(o\text{-tolyl})\}\text{Cl}(\text{PPh}_3)_2(\text{CO})$  is unstable, in particular with respect to reductive elimination of  $\text{Hg}(o\text{-tolyl})_2$  giving  $\text{IrCl}(\text{PPh}_3)_2(\text{CO})$ . The complexes  $\text{IrRCl}_2(\text{PPh}_3)_2$  undergo reactions with acetate to give  $\text{IrRCl}(\eta^2\text{-O}_2\text{CCH}_3)(\text{PPh}_3)_2$  and silanes to give  $\text{IrHCl}(\text{SiX}_3)(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}, \text{Et}$ ). The reactivity of  $\text{Ir}(o\text{-tolyl})\{\text{Hg}(o\text{-tolyl})\}\text{Cl}(\text{PPh}_3)_2$  is significantly different, undergoing decomposition upon heating or treatment with acetate and no reaction with  $\text{HSiEt}_3$ .

## METALS IN THE ASCIDIACEA

A. L. van den Brenk and C. J. Hawkins

Department of Chemistry, The University of Queensland

All components of the marine ecological system are affected by metals from both natural sources and pollution. Ultratrace levels ( $< 1$  ppb) of metal ions in sediments or water can result in the accumulation of these metals by both the flora and fauna through direct assimilation of the metal ions or through their food chains. Some of these metals have an essential role, some have a toxic effect, while others appear to be neither essential or toxic at the concentrations at which they are found.

Certain species of ascidians, benthic invertebrates from the phylum Chordata, have been known since 1911 to accumulate vanadium in very high concentrations ( $> 1000$  ppm dry wt.). Since that time, other metals such as iron, titanium, chromium, manganese, copper, zinc, niobium and tantalum have been found at significant concentrations.

The Hawkins group has been studying vanadium and iron in the Ascidiacea for some years. Some of the chelates isolated have had other metals coordinated. Consequently, the concentrations of a wide range of metals have been determined by ICP-MS for a number of aplousobranch species, particularly in the family Didemnidae.

This paper will report the results of the analyses, and relate the findings to what is known about other filter-feeding organisms, and to the types of chelates that have been found in the ascidians.

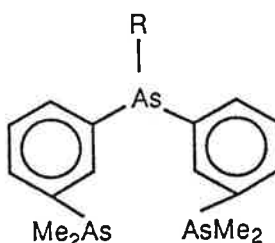
# Electrochemistry of Nickel(II)-Arsine Complexes: The Electron-Transfer Series $[\text{Ni}(\text{L}_3)_2]^{+4/+3/+2/+1/0}$ .

Alison J. Downard,<sup>a</sup> Lyall R. Hanton<sup>b</sup> and Rowena L. Paul<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

<sup>b</sup> Department of Chemistry, University of Otago, Dunedin, New Zealand.

Cyclic voltammetry in acetonitrile of the five-coordinate complexes  $[\text{Ni}(\text{L}_3)_2]^{2+}$  ( $\text{L}_3 = \text{mtas}$ ,  $\text{ptas}$ )

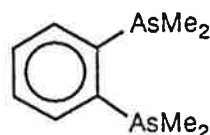


$\text{R} = \text{Me}$  '  $\text{mtas}$

$\text{R} = \text{Ph}$   $\text{ptas}$

reveals the reversible electron-transfer series  $[\text{Ni}(\text{L}_3)_2]^{+4/+3/+2/+1/0}$ .

By comparison with the electrochemical behaviour of  $\text{Co}(\text{mtas})_2^{2+}$  and  $\text{Ni}(\text{diars})(\text{mtas})_2^{2+}$  in acetonitrile and dichloromethane, all electron transfers



diars

are assigned as metal-based. The title complexes are thus the first nickel complexes to exhibit the complete electron-transfer series and the Ni(III) and Ni(IV) complexes are the first to incorporate the  $\text{NiAs}_6$  coordination sphere.

The ability of the tridentate arsine ligands to stabilise the lower and higher oxidation states of nickel can be rationalised by consideration of their electronic and structural properties.

## Putting Polyhedra into PEEK-type Polymers

H.M. Colquhoun<sup>†</sup>, J.A. Daniels<sup>††</sup>, M. Fox\*, J.A.H. MacBride\*,  
I.R. Stephenson\*<sup>††</sup> and K. Wade\*

ICI plc Runcorn<sup>†</sup>, Wilton<sup>††</sup>; Chemistry Department, Durham University\*, U.K.

Polymers in which para-disubstituted benzene rings are linked through alternating ether and ketone functions, such as polyetherketones  $\{C_6H_4OC_6H_4CO\}_n$  (PEK) or polyether-ether-ketones  $\{C_6H_4OC_6H_4OC_6H_4CO\}_n$  (PEEK) are among the most thermally stable organic polymers known, and are finding application in composite materials for specialist applications that exploit their thermal stability and low reactivity. Since icosahedral carborane units have many features in common with benzene rings - they are effectively 3-dimensional aromatic systems whose carbon derivative chemistry resembles that of benzene - and are thermally very robust, decomposing only above ca. 600°C, it appeared profitable to prepare analogues of PEEK and PEK in which disubstituted benzene rings were replaced by disubstituted  $C_2B_{10}$  icosahedral units, in a search for materials suitable for high temperature uses.

Our studies on carboranyl ethers  $(RO)_2C_2B_{10}H_{10}$  and ketones  $(RCO)_2C_2B_{10}H_{10}$  have shown such systems to be too susceptible to nucleophilic attack to allow the synthesis of useful polymers in which ether or ketone units were directly bonded to carborane icosahedra. However interpolation of a para-disubstituted benzene ring between the carborane icosahedron and an ether or ketone function leads to chemically far more robust species suitable for polymer synthesis. We have therefore prepared compounds 1,2- and 1,7- $C_6H_5OC_6H_4(CB_{10}H_{10}C)C_6H_4OC_6H_5$  and  $HO_2CC_6H_4(CB_{10}H_{10}C)C_6H_4CO_2H$  from which, either reacting with each other or with  $HO_2CC_6H_4C_6H_4CO_2H$ ,  $HO_2CC_6H_4OC_6H_4OC_6H_4CO_2H$  or  $C_6H_5OC_6H_4C_6H_4OC_6H_5$  in acid solution, it has proved possible to prepare PEEK or PEK type polymers. Details are given on our poster.



# Determination of Paramagnetic Susceptibility of Solid Micro-Samples by Proton NMR

Akiko Furuhashi, Isao Ono, and Akira Yamasaki\*

Aoyama Gakuin University, Morinosato-Aoyama, Atsugi 243-01, Japan

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A novel NMR technique for determining the magnetic susceptibility of very small-sized solid samples has been established.

NMR has long been used to determine the magnetic susceptibility of a small amount of paramagnetic material. Previous techniques have mostly applied only to samples in solution. We have established an effective new technique for solid micro-samples.

**Experimental.** A capillary of about 0.6 mm outer diameter containing about 2 ml of crystalline sample (no indicator) was set coaxially into an ordinary 5 mm NMR sample tube filled with deuterio-chloroform containing 1 % TMS. NMR spectra were recorded by the ordinary technique using the JEOL JNM-GX270 FT-NMR spectrometer.

**Results and Discussion.** When the capillary was empty, or when a diamagnetic sample was present, only two sharp proton signals were observed due to the TMS and its  $\text{CHCl}_3$  in the outer tube. Upon placing small fragments of paramagnetic crystal (about 2 mg) were placed in the capillary, two equally-shifted satellite signals appeared on the low-frequency side of the main peaks as shown in Fig. 1. The molar frequency difference proved to be proportional to  $n(n+2)$  ( $n$ : number of unpaired electrons) as shown in Fig. 2. This phenomenon appears to be recognized due to an induced magnetic field in the sample itself, which affects those protons of the standard attached to the outer wall of the inner capillary.

A different assignment analysis has been done here from those for liquid techniques. The described phenomenon was later found to be just observable at 60 MHz, but not at all clearly. Recent development of superconduction NMR has made possible such a new technique as presented here.

More details will be presented at the forthcoming Conference.

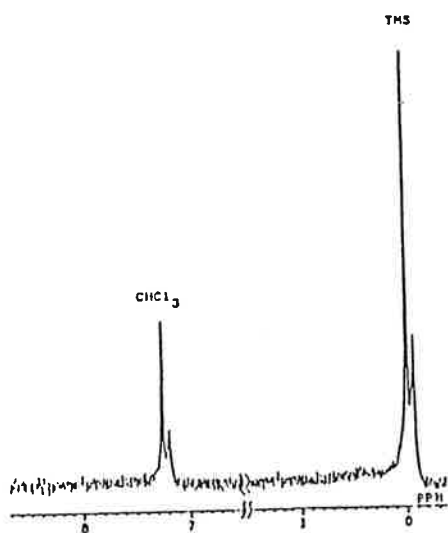


Fig. 1. 270 MHz Proton NMR spectra of  $\text{CDCl}_3$  (1% TMS) containing paramagnetic sample in capillary.  $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ , 0.62 mg ( $1.69 \times 10^{-4}$  mol); Hz: Benzimidazole

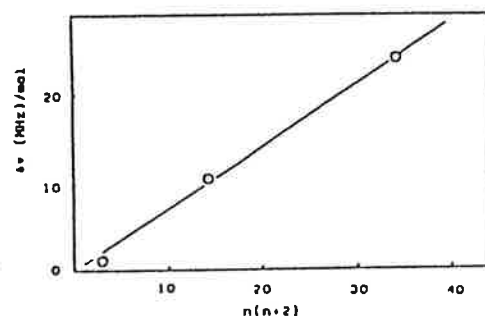


Fig. 2. The relation between  $\Delta\nu/\text{mol}$  and  $n(n+2)$ .  $n$ : number of unpaired electrons.

# OXIDATIVE DECARBONYLATION OF $[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_3]^-$ BY TETRA-ALKYLTHIURAM DISULFIDES: THE PROFUSION OF PRODUCTS!

Charles G. YOUNG,<sup>a</sup> Michael A. Bruck,<sup>b</sup> Michael Carducci<sup>b</sup> and John H. Enemark<sup>b</sup>

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The products of the reaction of  $[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_3]^-$  [ $\text{HB}(\text{Me}_2\text{pz})_3^-$  = hydrotris(3,5-dimethylpyrazolyl)borate anion] with tetraalkylthiuram disulfides in hot ( $> 60^\circ\text{C}$ ) acetonitrile are described; redox, decarbonylation and ligand rearrangement and fragmentation processes account for the formation of numerous products. Partial oxidative decarbonylation initially produced seven-coordinate  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_2(\text{S}_2\text{CNR}_2)$  (1), followed by the mixed-valence thiocarboxamido complex  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}^{\text{II}}(\text{CO})_2(\mu\text{-S})\text{W}^{\text{IV}}(\text{S}_2\text{CNR}_2)_2(\text{SCNR}_2)$  (2). Complete oxidative decarbonylation and ligand rearrangement/fragmentation resulted in the ultimate formation of complexes such as  $[\text{W}(\text{S}_2\text{CNR}_2)_4]^+$ ,  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WS}(\text{S}_2\text{CNR}_2)$  (3) and  $\text{W}_2(\mu\text{-S})_2(\mu\text{-S}_2\text{CNR}_2)_2(\text{S}_2\text{CNR}_2)_2$ . Isolation and characterization of the products including the X-ray structures of (1), (2) and (3) (where  $\text{R} = \text{Et}$ ) will be described.

# MOLYBDENUM-SULFUR AND OXYGEN ATOM TRANSFER CHEMISTRY OF RELEVANCE TO MOLYBDOENZYMES

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We have been pursuing the chemistry of high-valent molybdenum complexes of the sterically encumbered hydrotris(3,5-dimethylpyrazolyl)borate ligand,  $\text{HB}(\text{Me}_2\text{pz})_3^-$ , in attempts to develop models of the active site of the oxo-type molybdoenzymes xanthine oxidase and xanthine dehydrogenase. We report the synthesis, oxygen atom transfer kinetics and catalytic properties of the oxo-Mo(IV) and dioxo-Mo(VI) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\eta^2\text{-S}_2\text{PR}_2)$  (1) and  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2(\eta^1\text{-S}_2\text{PR}_2)$  (2), respectively. Sulfurization of these complexes, one possible route to models of the  $[\text{MoOS}]^{2+}$  enzyme active sites, will be described. Synthetic, spectroscopic and X-ray crystallographic studies of molybdenum complexes such as 1, 2,  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoS}(\mu\text{-S})_2\text{MoS}(\text{S}_2\text{PPr}^i_2)$ ,  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{S}_3\text{PPr}^i_2)$ ,  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{S}_3\text{P}(\text{OR})_2)$  and  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoS}(\text{Cl})(\text{S}_2\text{PPr}^i_2)$  will be presented.

## ORGANOMETALLIC OXO-MOLYBDENUM AND OXO-TUNGSTEN COMPLEXES

Aston A. EAGLE,<sup>a</sup> S.G. Feng,<sup>b</sup> Maureen F. Mackay,<sup>a</sup> Joseph L. Templeton,<sup>b</sup> Peter White,<sup>b</sup> and Charles G. Young<sup>a</sup>

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We are exploring the synthesis and chemistry of organometallic oxo complexes of Mo and W due to the relevance of such species to the transformation of organics upon metal oxide surfaces. In this regard, we are particularly interested in oxo(alkyl), oxo(carbonyl) and oxo(olefin) complexes. The reactions of oxo-Mo complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{X}$  and  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOX}_2$  [ $\text{HB}(\text{Me}_2\text{pz})_3^-$  = hydrottris(3,5-dimethylpyrazolyl)borate anion, X = halide] with Grignard reagents will be described. Reactions involving  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}_2\text{Cl}$  result in the formation of the novel mixed-valence complex  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}^{\text{VO}}(\text{Cl})(\mu\text{-O})\text{Mo}^{\text{VI}}\text{O}_2\{\text{HB}(\text{Me}_2\text{pz})_3\}$  (1) as the major product while reactions involving  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOCl}_2$  appear to produce isolable oxo(alkyl) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoOR}_2$ . Oxidative hydrolysis of  $[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_3]^-$  results in the formation of mixed-valence  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}^{\text{IVO}}(\text{CO})(\mu\text{-O})\text{W}^{\text{VI}}\text{O}_2\{\text{HB}(\text{Me}_2\text{pz})_3\}$  (2) while aerial oxidation of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_3\text{X}$  (X = Cl, Br) complexes results in the formation of rare mononuclear oxo(carbonyl) complexes  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WO}(\text{CO})\text{X}$  ((3), X = I). The synthesis and spectroscopic properties of the complexes and the X-ray crystal structures of (1), (2) and (3) will be presented.

# NMR STUDY OF TRANS-DIAMMINE PLATINUM(II) COMPLEXES OF SIMPLE OXYGEN-DONOR LIGANDS

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There has been a lot of interest in the chemistry of *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> due to its anti-tumor activity. The *trans* isomer is inactive and as such its chemistry has been relatively ignored.

A method of preparation of *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> has been perfected which allows <sup>15</sup>N-enriched ammonia to be used conveniently and with high yields. When <sup>15</sup>N-enriched ligands are used <sup>15</sup>N and <sup>195</sup>Pt N.M.R. spectroscopy are powerful tools for characterising platinum ammine complexes in solution. As has been demonstrated with the *cis* isomer.<sup>1</sup>

*Trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> is reacted with AgNO<sub>3</sub> at 90°C for 48 hours to produce *trans*-[Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>. The reactions of *trans*-Pt(<sup>5</sup>NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> with some simple oxygen-donor ligands (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, <sup>-</sup>OCOCH<sub>3</sub>, and PO<sub>4</sub><sup>3-</sup>) have been investigated. These reactions are generally slow due to the low trans influences of the ligands involved. Mono and Bis complexes have been characterised and in some cases bridging has been identified. The acid dissociation constants for *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> and *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl(H<sub>2</sub>O)<sup>+</sup> have also been determined.

1. T.G. Appleton, J.R. Hall, S.F. Ralph, and C.S.M. Thompson, *Inorg. Chem.* 1989, 28, 1989 and references therein.

# METAL COMPLEXES OF AN ENCAPSULATING LIGAND WITH THE UNSYMMETRICAL $N_4S_2$ DONOR SET.

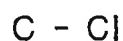
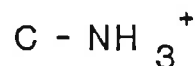
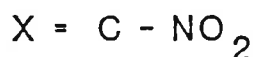
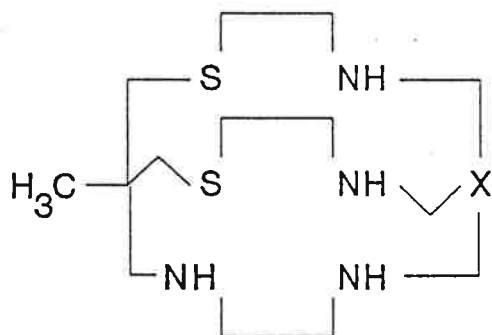
Therese M. Donlevy,<sup>1</sup> Lawrence R. Gahan,<sup>1</sup> Trevor W. Hambley<sup>2</sup>

1. Chemistry Department, University of Queensland, Brisbane, QLD 4072.
2. Chemistry Department, University of Sydney, Sydney, NSW 2006.

The unsymmetrically substituted ligand 5-(4-amino-2-azabutyl)-5-methyl-3,7-dithianonane-1,9-diamine has been successfully employed as a precursor for the preparation of encapsulated complexes of cobalt(III). Complexes with the capping groups  $-NO_2$ ,  $-NH_3^+$ ,  $-Cl$  and  $-H$ , as well as the aza capped complex, have been prepared and characterized. The electron transfer properties of these complexes have been explored and cross reactions with other hexaaza-encapsulated complexes studied.<sup>1</sup> As well, self exchange rates of electron transfer have been measured using NMR line broadening methods.<sup>2</sup>

This type of encapsulated complex of cobalt exhibits behaviour intermediate between the  $N_6$  and  $N_3S_3$  encapsulated complexes in terms of  $\epsilon^0$  for the cobalt(III/II) couples, but the rates for electron transfer are more indicative of the mixed thioether-nitrogen type cage complexes.<sup>1-4</sup>

Removal of the metal ion, as cobalt(II), from the  $NH_3^+$  capped cage results in an encapsulating ligand containing  $N_4S_2$  donors. The ligand reacts readily with other metal ions such as copper(II), nickel(II), and zinc(II) to form the corresponding encapsulated metal complexes. The copper(II) complex has been structurally characterized as a 2+2+2 distorted octahedron.



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## COBALT COMPLEXES OF THE CYCLONONANE LIGANDS

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The ligands 1,4,7-triazacyclononane (9aneN<sub>3</sub>), 1-thia-4,7-diazacyclononane (9aneN<sub>2</sub>S), and 1,4,7-trithiacyclononane (9aneS<sub>3</sub>) form octahedral complexes with cobalt(III). The ligands are of interest because the variations possible permit the preparation of complexes with chromophores N<sub>6-x</sub>S<sub>x</sub>, x = 0,1,2,3,4,6. The complexes [Co(9aneN<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>, [Co(9aneN<sub>2</sub>S)<sub>2</sub>]<sup>3+</sup>, [Co(9aneN<sub>3</sub>)(9aneS<sub>3</sub>)]<sup>3+</sup>, [Co(9aneS<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>, and [Co(9aneN<sub>3</sub>)(9aneN<sub>2</sub>S)]<sup>3+</sup> have been prepared previously.<sup>1-4</sup> As well, the cobalt(II) complexes [Co(9aneN<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> and [Co(9aneS<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> have been characterized.<sup>5,6</sup> We have studied the EPR spectra of the cobalt(II) complexes of a range of these complexes. As well, the cobalt-59 NMR spectra of the cobalt(III) complexes have been investigated.

The EPR study (X band, 120 K and 4 K) in aqueous solution of the cobalt(II) complexes of these ligands indicates a relationship between the ligand field strength and  $g_{av}$ , such that for a weaker ligand field strength the g values are shifted to lower field. As well, studies in dimethylformamide of complexes containing 9aneN<sub>2</sub>S indicate possible ligand dissociation.

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1-THIA-4,7-DIAZACYCLONONANE (9aneN<sub>2</sub>S) COMPLEXES OF IRON(III)

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2. Chemistry Department, University of Sydney, Sydney, NSW 2006.

The ligand 1,4,7-triazacyclononane (9aneN<sub>3</sub>) has in recent years been successfully employed to model the spectroscopic and magnetic properties of biomolecules, in particular dimeric and oligomeric clusters with the  $\mu$ -oxo and bis( $\mu$ -carboxylato) core.<sup>1</sup> The chemistry of the iron(II) and iron(III) complexes of the mono-thia analogue of 9aneN<sub>3</sub>, that is 1-thia-4,7-diazacyclononane (9aneN<sub>2</sub>S),<sup>2,3</sup> has however not been explored. Until now lack of a convenient synthesis of the ligand has restricted the scope of studies with this ligand.

This paper presents the synthesis and characterization of the mononuclear  $\mu$ -oxo iron(III) and binuclear bis( $\mu$ -carboxylato)iron(III) complexes of 9aneN<sub>2</sub>S.

Comparisons with the 9aneN<sub>3</sub> complexes will be drawn.

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3. L.R.Gahan, T.W.Hambley, G.H.Searle, M.J.Bjerrum, E.Larsen; *Inorg. Chim. Acta.*, 1988, 147, 17-26.



AN  $^{15}\text{N}$  AND  $^{195}\text{Pt}$  NMR STUDY OF PLATINUM-NITRO COMPLEXEST.G. Appleton, K.J. Barnham, J.R. Hall and M.T. Mathieson

The final products of the reactions of  $\text{K}_2\text{Pt}(\text{NO}_2)_4$  with phosphoric and sulphuric acid are Pt(III) complexes which have been well characterized [1,2]. Less work has been done on Pt(III) acetates [3,4]. In all these reactions, little is known as to how these complexes form. The complexes  $\text{Pt}_2(\text{NO}_2)_4(\text{OH})_2^{2-}$  and  $\text{Pt}_4(\text{NO}_2)_9\text{O}_3^{5-}$  have been proposed as intermediates in the reactions of  $\text{K}_2\text{Pt}(\text{NO}_2)_4$  with sulphuric acid [5].

The initial stages of the reactions of  $\text{K}_2\text{Pt}(\text{NO}_2)_4$  with acids (viz.  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{CH}_3\text{COOH}$ ) have been studied using  $^{195}\text{Pt}$  and  $^{15}\text{N}$  NMR spectroscopy, using  $^{15}\text{N}$  labelled nitrite starting materials. Acid attack on coordinated nitrite takes place initially yielding a trinitro complex followed by coordination of the anionic ligand (not  $\text{ClO}_4^-$ ).

The complex  $\text{K}_2[(\text{NO}_2)_2\text{Pt}(\mu\text{-OAc})_2\text{Pt}(\text{NO}_2)_2]\cdot\text{H}_2\text{O}$  has been isolated in small yields from such a reaction. Such compounds can be oxidized to dimeric Pt(III) complexes [6].

The reactions of nitro-aqua complexes have also been examined by this method.

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A COURSE IN INORGANIC TOXICOLOGY:

"CAN INORGANIC CHEMISTS MAKE A POSITIVE CONTRIBUTION?"

Colin Rix, Victoria University of Technology,

RMIT 124 La Trobe Street,

Melbourne, Australia

Traditional Inorganic Chemistry courses stress the importance of complexing, acid-base, redox and solubility principles in providing an understanding of main-group and transition-metal chemistry.

On the other hand, toxicology courses are based on biochemistry and tend to emphasize the toxicokinetics of organic molecules in biological systems. This is unfortunate, since it omits to discuss a large number of potentially toxic inorganic materials which are likely to be encountered in the workplace.

At RMIT I have developed an Inorganic Toxicology course which attempts to combine these two disparate topic areas into a meaningful discussion of the toxicity associated with Inorganic materials.

Clearly an inter-disciplinary approach is necessary which demands not only a person competent in Inorganic Chemistry, but also one who has a good command of the Life Sciences, particularly physiology and biochemistry.

Nevertheless, the effort is worthwhile, since the inorganic chemist can fill a gap which is often left by the physiologist or biochemist teaching toxicology.

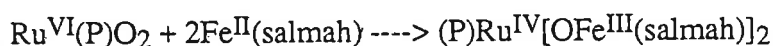
## SYNTHESIS OF OXO RUTHENIUM PORPHYRIN COMPLEXES

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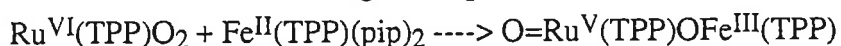
Oxo bridged heterobinuclear compounds of the type  $(\text{TPP})\text{CrOM}(\text{Lig})^1$  have been prepared by the redox reaction of  $\text{Cr}^{\text{IV}}\text{O}(\text{TPP})$  and iron(II), manganese(II) and molybdenum(IV) complexes containing ligands such as salicylaldimines, dithiocarbamates and porphyrins. Similarly the reaction between the high valent  $\text{Mo}(\text{VI})$  dioxo species  $(\text{dtc})_2\text{Mo}^{\text{VI}}\text{O}_2$  and other low valent metal complexes ( $\text{Fe}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Cr}^{\text{II}}$ ) also led to the formation of heterobinuclear oxobridged compounds:  $(\text{dtc})_2\text{Mo}^{\text{V}}(\text{O})\text{OM}(\text{Lig})$ .<sup>1</sup> It was thought that the high valent trans dioxo ruthenium(VI) porphyrin  $\text{Ru}^{\text{VI}}(\text{P})\text{O}_2^2$ , like  $\text{Cr}^{\text{IV}}\text{O}(\text{TPP})$  and  $\text{Mo}^{\text{VI}}(\text{O})_2(\text{dtc})_2$  could also be reactive towards low valent metal species and form di- or trinuclear oxobridged compounds:  $(\text{P})\text{Ru}^{\text{IV}}[\text{OM}(\text{Lig})]_2$ ,  $(\text{P})\text{Ru}^{\text{V}}(\text{O})\text{OM}(\text{Lig})$ .

$\text{Ru}(\text{P})\text{O}_2$  ( $\text{P} = \text{OEP}, \text{TPP}^3$ ) reacts with  $\text{Fe}(\text{salmah})^3$  in dry  $\text{CH}_2\text{Cl}_2$  or toluene to give the mixed metal trinuclear oxobridged compound, which can be precipitated from the reaction mixture with hexane.



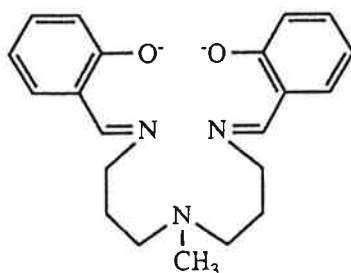
Preliminary investigation of the magnetic properties of these compounds suggests that the ruthenium metal centre is low spin  $d^4$  and little or no coupling occurs between the high spin  $d^5$  iron centres ( $\mu_{\text{eff}} = 8.3\text{BM}$ ).

When  $\text{Ru}(\text{TPP})\text{O}_2$  reacts with  $\text{Fe}(\text{TPP})(\text{pip})_2$  in dry  $\text{CH}_2\text{Cl}_2$  immediate precipitation of the heterobinuclear oxobridged compounds occurs.



Magnetic data indicates that strong ferromagnetic coupling occurs between the low spin  $d^3$  ruthenium centre and the high spin  $d^5$  iron centre ( $\mu_{\text{eff}} = 6.9\text{BM}$ ).

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OEP = 2,3,7,8,12,13,17,18 octaethyl porphyrinate(-2).  
salmah = N,N'-4-methyl-azaheptane-1,7-diylbis(salicylidenimine)(-2).



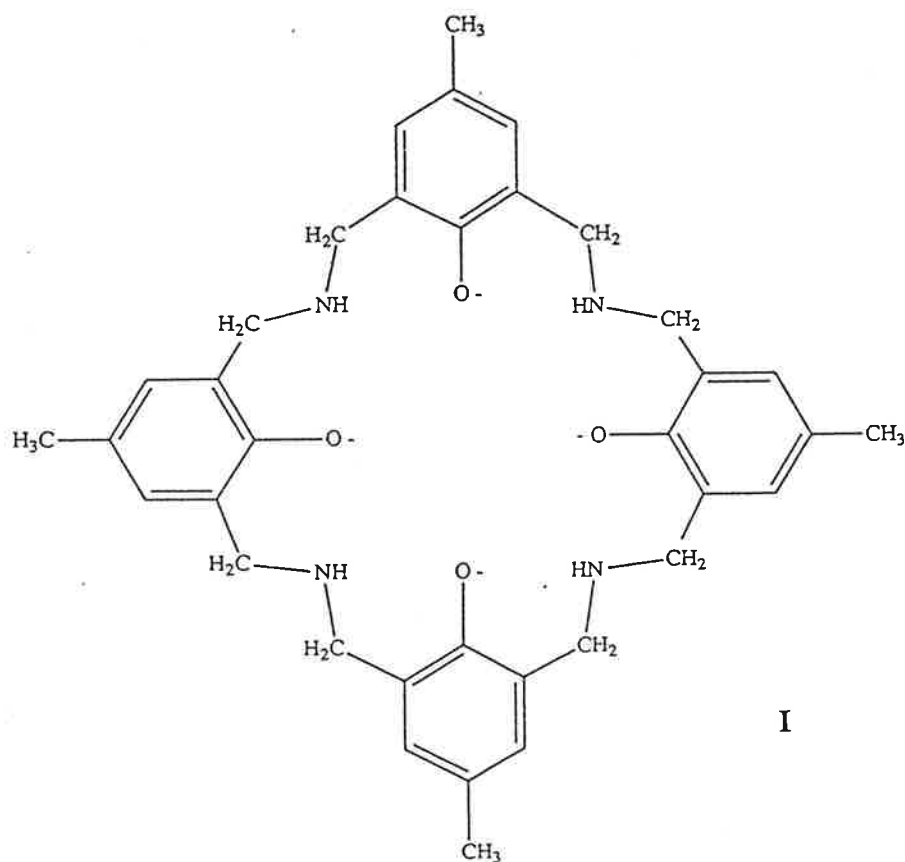
## COMPLEXES OF A NEW TETRANUCLEATING MACROCYCLIC LIGAND

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Recent research into transition metal complexes of macrocyclic ligands capable of binding up to four metal centres in close proximity has focussed on tetra-Schiff base ligands. The susceptibility of Schiff base compounds towards hydrolysis complicates their application in aqueous media. A more flexible and stable ligand framework is obtained by reduction of the imine ( $\text{CH}=\text{N}$ ) linkages of Schiff bases to amine ( $\text{CH}_2-\text{N}$ ) linkages.

A new, tetra-amino-tetra-phenolic macrocyclic ligand  $\text{L}^{4-}$  (I) has been prepared and characterised as its tetrahydrochloride salt. The x-ray crystal structures of the metal-free ligand, two tetranuclear complexes ( $\text{Zn}_4$  and  $\text{Cu}_4$ ) and one trinuclear complex ( $\text{Co}_3$ ) of (I) will be presented.



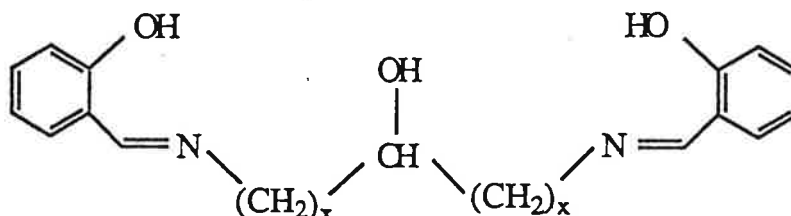
# A BINUCLEAR IRON(III) COMPLEX WITH INEQUIVALENT METAL ENVIRONMENTS

Gary D. Fallon, Keith S. Murray and Thao Quach

*Chemistry Department, Monash University, Clayton, Victoria 3168, Australia*

Binuclear complexes of iron continue to attract attention not only from the magnetostructural point of view but also because of their use as models for iron-oxo proteins (e.g. hemerythrins (Hr), ribonucleotide reductase (RR), purple acid phosphatase (PAP) and methane monooxygenase (MMO)) and as catalysts for organic oxidations and epoxidations. A variety of bridging core units have been structurally characterized in recent years containing  $\mu$ -oxo/hydroxo/alkoxo/carboxylato combinations within binuclear or higher nuclearity clusters. Two broad synthetic strategies have emerged i.e. use of co-ligands which allow formation of "unsupported" bridges across vacant sites on neighbouring Fe atoms, or, use of binucleating co-ligands which provide built in "supported" bridges usually of the alkoxo or phenoxo type. The work described here is of the latter type.

A range of interesting binuclear Fe(III) complexes of types  $[\text{FeL}^1]_2 \cdot \text{THF}$ ,  $[\text{Fe}_2\text{L}^1(\text{OMe})(\text{Cl})_2(\text{MeOH})]$ ,  $[\text{FeL}^2]_2 \cdot \text{DMF}$ , and  $[\text{Fe}_2\text{L}^2(\text{OH})(\text{Cl})_2]$  have been synthesized using the Schiff-base ligands shown below. The results of X-ray crystal



$$x = 1 ; \text{L}^1 \text{H}_3$$

$$x = 2 ; \text{L}^2 \text{H}_3$$

structure studies, magnetic, Mössbauer and electrochemical measurements will be described. The iron coordination geometries in the doubly-bridged complex  $[\text{Fe}_2\text{L}^1(\text{OMe})(\text{Cl})_2(\text{MeOH})]$  are inequivalent, one being 5-coordinate the other 6-. This is a rare situation in model studies and is reminiscent of the situation in the Hr protein active site.

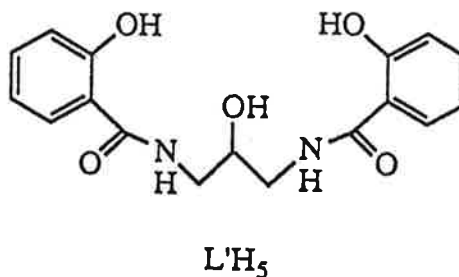
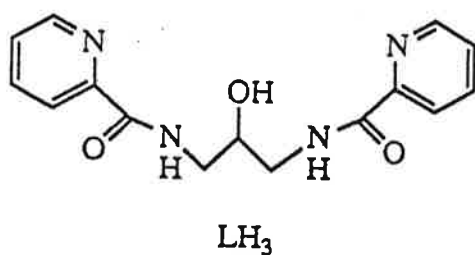
# NEW BINUCLEATING AMIDE LIGANDS AND THEIR COPPER(II) AND MANGANESE(III) COMPLEXES

Karen Bertoncello, Gary D. Fallon and Keith S. Murray\*

*Chemistry Department, Monash University, Clayton, Victoria 3168, Australia*

Reactions of functionalized diamines such as 1,3-diamino-propan-2-ol with an appropriate acid chloride or - ester precursor leads to the formation of binucleating amide ligands of the types shown below. These ligands have the dual capabilities of stabilizing high oxidation states of metal ions and of forming binuclear moieties, perhaps of the mixed-valent type. These are desirable features when attempting to model aspects of the polynuclear metallosites in biomolecules of copper, iron and manganese. The chemistry of these acid-amide ligands also shows some similarities to that of peptide-metal interactions.

The syntheses, structures, magnetic and redox properties of a range of mononuclear and binuclear complexes of copper(II) and manganese(III) will be described. In the case of Mn(III) one of the few examples of doubly bridged  $\mu$ -alkoxo- $\mu$ -acetato complexes will be presented.

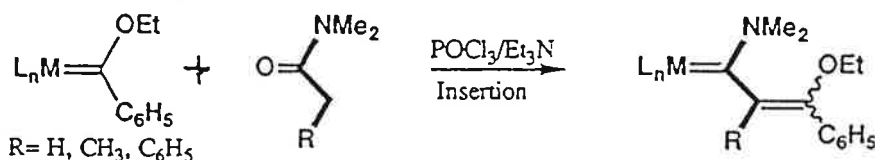


# CONDENSATION REACTIONS OF ACID AMIDES WITH TRANSITION METAL CARBENE COMPLEXES

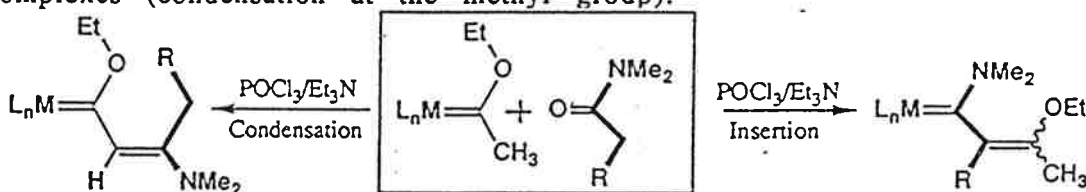
1) R. Aumann, 2) P. Hinterding

1) Organisch-Chemisches Institut der Universität Münster, Orleans-Ring 23, 4400 Münster, Germany. 2) Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide 5001, South Australia

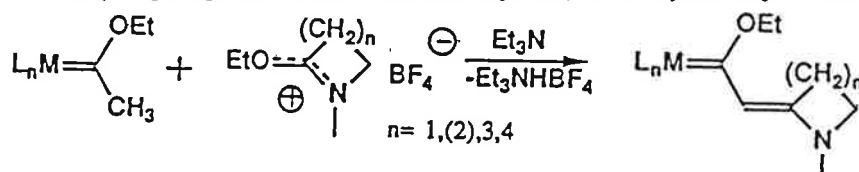
Novel reactions to build up C=C bonds, conjugated with  $L_nM=C$  bonds ( $L_nM$ :  $(CO)_5Cr$ ,  $(CO)_5Mo$ ,  $(CO)_5W$ ), are presented. Arylethoxycarbene complexes and tertiary amides react under the influence of  $POCl_3/Et_3N$  with condensation by insertion of a  $C_2$ -unit into the  $M=C$  bond to form (E/Z)-amino alkenyl carbene complexes.



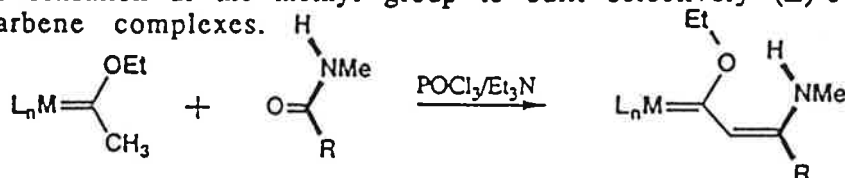
Methylethoxycarbene complexes under the same conditions give (E/Z)-aminoalkenyl carbene complexes as well as (E)-ethoxyalkenyl carbene complexes (condensation at the methyl group).



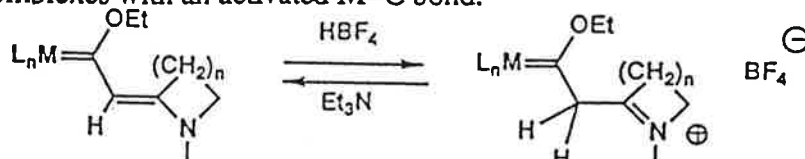
Methylethoxycarbene complexes react with amidium salts by condensation at the methyl group to form exclusively (E)-ethoxyalkenyl carbene complexes.



Methylethoxycarbene complexes react with secondary amides by condensation at the methyl group to build selectively (Z)-ethoxyalkenyl carbene complexes.



The protonation of the ethoxyalkenyl carbene complexes gives novel cationic carbene complexes with an activated  $M=C$  bond.



Ref.: R. Aumann, P. Hinterding, Chem. Ber. 122 (1989) 365, R. Aumann, P. Hinterding, ibid. 123 (1990) 611, R. Aumann, P. Hinterding, ibid. 123 (1990) 847.

# SYNTHESIS OF OXO- AND ORGANOIMIDO-BRIDGED COMPLEXES OF (TETRAMETHYLDIBENZOTETRAAZA[14]ANNULENE)IRON(III)

Peter J. Nichols, Gary D. Fallon and Bruce O. West

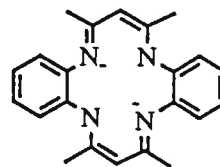
Department of Chemistry, Monash University, Clayton, Victoria, Australia, 3168

Many iron(II) chelate complexes have been found to be readily oxidised by dioxygen to yield homobimetallic oxo-bridged complexes<sup>1</sup>. Heterobimetallic oxo-bridged species have also been prepared via the reactions between metal oxo complexes and iron(II) chelates<sup>1</sup>. Iron(II) Schiff base complexes have also been found to react with arylazides to give homobimetallic arylimido-bridged species<sup>2</sup>. We have now observed that the macrocyclic Schiff base complex, Fe(tmtaa)<sup>3</sup>, can also be oxidised to yield homo- and hetero-bimetallic, oxo- and arylimido-bridged complexes.

Goedken *et al.*<sup>4</sup> found that the addition of dioxygen to acetonitrile solutions of Fe(tmtaa) results in the formation of [Fe(tmtaa)]<sub>2</sub>O·CH<sub>3</sub>CN. Similarly we have found that [Fe(tmtaa)<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>] precipitates from toluene solutions of Fe(tmtaa) layered with hexane. Unlike the acetonitrile adduct, the latter complex is quite soluble in organic solvents and is readily hydrolysed. Fe(tmtaa) is also readily oxidised by (TPP)CrO<sup>3</sup> to form the heterobimetallic oxo-bridged complex, (TPP)CrOFe(tmtaa) which exhibits similar properties to other (TPP)CrOFe(L) complexes<sup>1</sup>.

Fe(tmtaa) also reacts with arylazides in toluene to form arylimido-bridged complexes, [Fe(tmtaa)]<sub>2</sub>NAr. Thus, when Fe(tmtaa) was mixed with *p*-methoxyphenylazide in dry toluene, the initial blue/violet solution rapidly changed to brown and dinitrogen was evolved. The addition of hexane resulted in the precipitation of a dark brown crystalline product which analysed as [Fe(tmtaa)]<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>. Heterobimetallic arylimido-bridged complexes can also be prepared in an analogous procedure to that employed in the synthesis of oxo-bridged complexes via the use of the chromium(IV) organoimido porphyrin complexes, (TPP)CrNAr<sup>5</sup>.

1. B. O. West, *Polyhedron*, **8**, 219 (1989).
2. P. J. Nichols, G. D. Fallon, K. S. Murray and B. O. West, *Inorg. Chem.*, **27**, 2795 (1988).
3. tmtaa: dianion of tetramethyldibenzotetraaza[14]annulene



- TPP: dianion of 5,10,15,20-tetraphenylporphyrin
4. V. L. Goedken and Y.-A. Park, *J. Chem. Soc., Chem. Commun.*, 214 (1975).
5. R. L. Elliott, P. J. Nichols and B. O. West, *Polyhedron*, **6**, 2191 (1987).



# SUBSTITUTION REACTION OF $\text{Ru}_3(\mu\text{-H})(\text{CO})_9(\text{C}_{12}\text{H}_{15})(\mathbf{1})$ WITH GROUP 15 LIGANDS

by

Omar bin Shawkataly<sup>a</sup>, Siang-Guan Teoh<sup>b</sup> and Hoong-Kun Fun<sup>c</sup>

<sup>a</sup> Chemical Sciences Programme, Centre for Off-Campus Studies,

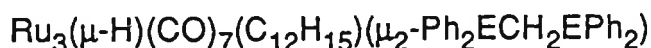
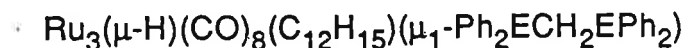
<sup>b</sup> School of Chemistry

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Universiti Sains Malaysia, 11800, Minden, Penang, Malaysia

The substitution of  $\text{Ru}_3(\text{CO})_{12}$  with Group 15 ligands have been extensively studied<sup>1</sup>. The substitution reaction of **(1)** with  $\text{PMe}_2\text{Ph}$ ,  $\text{P}(\text{OMe})_3$  and  $\text{P}(\text{OMe}_2)_3\text{CEt}$  have been reported<sup>2</sup>. We have decided to reexamine the reaction of **(1)** with Group 15 ligands especially bidentate tertiary phosphines and arsines.

Reaction of **(1)** with  $\text{Ph}_2\text{ECH}_2\text{EPh}_2$  (where E = P or As) yield 3 products, only 2 of these have been fully characterised.



The structure of the P and As analogue is isomorphous.

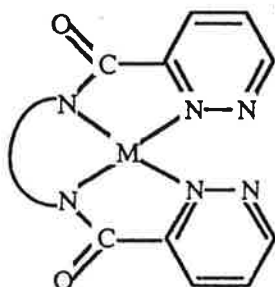
The characterisation and the single crystal X-ray studies and the chemistry of the products will be presented.

1. M.I. Bruce, J.G. Matison and B.K. Nicholson, *J. Organomet. Chem.*, 247, 321 (1983).
2. M.I. Bruce, M.A. Cairns and M. Green, *J. Chem. Soc., Dalton Trans.*, 1293 (1972).

# LIGAND BEHAVIOUR OF METAL BIS-PYRIDAZINECARBOXAMIDE COMPLEXES

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School of Chemistry, University of New South Wales, Kensington, NSW 2033,  
Australia

Bis-pyridazinecarboxamide ligands, based on diamines, generally produce metal complexes with structures of the type shown.



We find that such metal bis-pyridazinecarboxamides can act as NN-donors to other metallic systems producing dimeric and trimeric pyridazine-bridged complexes. Alternatively, O,O-coordination *via* the amide oxygens can produce polymeric structures.<sup>1,2</sup>

The magnetic, spectroscopic, and X-ray structural properties of a range of bridged homo- and hetero-metallic complexes, based on metal bis-pyridazinecarboxamides, are described, together with results involving other bis-carboxamide systems.<sup>1,2</sup>

1. M.A.A. Miah and D.J. Phillips, *Inorg. Chim. Acta*, 165 (1989) 23
2. D.J. Phillips *et al.*, manuscripts submitted for publication.

SYNTHESIS AND CHARACTERIZATION OF VANADIUM(III) COMPLEXES WITH SULPHUR LIGATION.

Norman S. Dean, Joe R. Rambo, John C. Huffman and George Christo  
Department of Chemistry, Indiana University, Bloomington, IN 47405, U.S.

Our continuing investigations into vanadium(III) sulphur chemistry have recently produced two interesting new areas of progress involving chelating ligands.  $\text{VCl}_3(\text{THF})_3$  has been employed as a convenient starting point and the chelating ligands are ethane-1,2-dithiolate ( $\text{edt}^{2-}$ ) and 2,2'-bipyridine (bipy). Treatment of  $\text{VCl}_3(\text{THF})_3$  with different ratios of  $\text{Na}_2\text{edt}$  has led to two mixed ligand V/edt/Cl complexes. These products have nuclearities of three and four and their structures will be described. In parallel reactions, treatment of  $\text{VCl}_3(\text{THF})_3$  with monodentate thiolates ( $\text{NaSR}$ ) and bipy has led to isolation of mixed ligand V/SR/bipy products. These materials have themselves proven useful as starting points for further chemistry, including the reaction with elemental sulphur which has produced novel V/S/bipy products. The structures and properties of these bipy-containing species will be described.

The preparation of some novel lanthanide organoamide complexes incorporating heterocyclic amide ligands, and a study of their characterization and properties.

Glen Deacon, Craig Forsyth and Carmel Tutton.

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

Synthesis of the lanthanide organoamides were carried out by ligand exchange reactions of bis(pentafluorophenyl)-europium or -ytterbium and the heterocyclic amines (1).



L = carbazole (cbzH), x=4; 2-phenylindole (pinH), x=4; 2-phenylindole (pbiH), x=2.5; benzotriazole (btzH), x=0.5.

Treatment of elemental lanthanides with  $\text{Hg}(\text{C}_6\text{F}_5)_2$  and pinH or 2,3,4,5-tetraphenylpyrrole (tppH) in tetrahydrofuran (thf) gives the divalent amide complexes  $\text{M}(\text{pin})_2(\text{thf})_4$  (M=Sm, Eu, Yb) and  $\text{M}(\text{tpp})_2(\text{thf})_3$  (M=Sm, Yb). Desolvation of  $\text{M}(\text{pin})_2(\text{thf})_4$  under vacuum gives  $\text{Yb}(\text{pin})_2(\text{thf})$  and  $\text{Sm}(\text{pin})_2(\text{thf})_3$ . Single crystal X-ray structure analyses of  $\text{Eu}(\text{cbz})_2(\text{thf})_4$  and  $\text{Yb}(\text{pin})_2(\text{diglyme})(\text{thf})$  (bis(2-methoxyethyl)ether=diglyme) show that these complexes are monomeric and six coordinate. The europium complex has a distorted octahedral stereochemistry with *cis*-cbz ligands. The geometry of the ytterbium complex is very irregular but can be approximated to a capped square base pyramid.

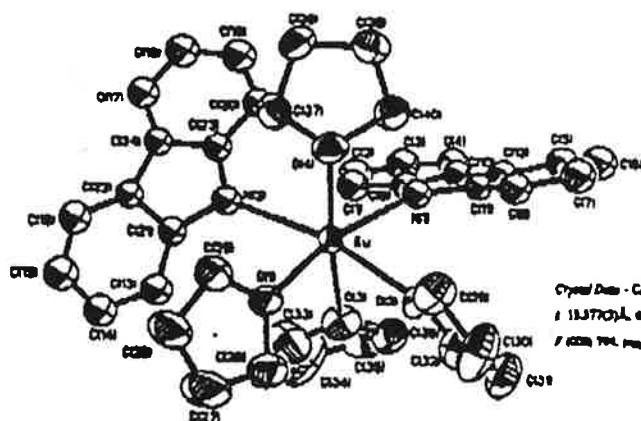


Figure 1.13. The molecular structure of  $\text{Eu}(\text{cbz})_2(\text{thf})_4$ .

Crystal Data:  $\text{C}_{24}\text{H}_{16}\text{F}_8\text{EuO}_4$ ,  $M_r$  772.8, orthorhombic, space group  $P2_1$ ,  $a$  9.992(12),  $b$  10.363(12),  $c$  13.377(12) Å,  $V$  1331(11) Å<sup>3</sup>,  $Z$  4,  $D_x$  1.61 g cm<sup>-3</sup>,  $D_m$  1.61 g cm<sup>-3</sup>,  $\mu$  1.91 mm<sup>-1</sup>.

Other amines have been investigated including 4,6-dimethoxy-2,3-diphenylindole (dmpiH) and diphenylamine (dpaH). The above ligands were reacted with elemental Yb and  $\text{Hg}(\text{C}_6\text{F}_5)_2$  to yield  $\text{Yb}(\text{dmpi})_2(\text{diglyme})_x$  ( $1 \leq x \leq 2$ ) and  $\text{Yb}(\text{dpa})_2(\text{diglyme})_2$ .

Investigation of a new synthetic route for the preparation of divalent organoamides by redox transmetalation of lanthanides with amidomercury compounds has been undertaken.

# A VIBRATIONAL SPECTROSCOPIC STUDY OF BONDING IN MIXED LIGAND GROUP VI TRANSITION METAL CARBONYLS

M. J. Aroney, R. S. Armstrong, M. S. Davies and K. W. Nugent.  
Department of Inorganic Chemistry, University of Sydney, Australia, 2006.

Compounds of the general formula  $LM(CO)_5$  where M is Cr, Mo or W, and L is  $PPh_3$ ,  $AsPh_3$ ,  $SbPh_3$ ,  $P(OCH_2)_3CCH_3$ ,  $PCl_3$ ,  $PBr_3$  and  $N(C_2H_4)_3CH$  have been prepared and studied by infrared and Raman spectroscopy in the regions  $100-500cm^{-1}$  and  $1800-2150cm^{-1}$ . Infrared spectra were recorded in both the solid and solution phases; Raman spectra were obtained only in solution. Cyclohexane was used as solvent except for the complexes in which the ligand L is  $P(OCH_2)_3CCH_3$ ; these were examined in tetrahydrofuran.

The study concentrated on the  $\nu(CO)$ ,  $\nu(MC)$  and  $\nu(ML)$  vibrations, particularly those of  $A_1$  symmetry. Spectral band frequencies and intensities were measured and analysed in terms of bond polarity (IR) and polarisability (R). These were interpreted in terms of  $\sigma$ - or  $\pi$ - bonding in M-L.

The results of the polarisability studies led to the conclusion that a strong  $\pi$ -interaction exists where L is  $PBr_3$ . In contrast, quinuclidine exhibits virtually no  $\pi$ -bonding capability with the metal. Tertiary aryl- phosphines, arsines and stibines have intermediate properties.

The variation in the nature of the M-L bond is small for the three triphenyl derivatives studied with each metal, although it appears that arsenic has the lowest  $\pi$ - accepting ability. Triphenylphosphine has a higher overall  $\sigma$ - donor,  $\pi$ - accepting capacity than do the arsenic and antimony analogues.

The role of the metal M in the M-L interaction is yet to be completely understood; molybdenum appears to be the least effective  $\pi$ - donating ligand in the triad.

The position of  $P(OCH_2)_3CCH_3$  in the  $\sigma$ - donor/  $\pi$ - acceptor series appears to be between that of the triaryl- phosphines, arsines and stibines and the strong  $\pi$ - bonding  $PBr_3$  ligand.

## ELECTROCHEMICAL STUDIES IN THE CLUSTER CATALYSED REDUCTION OF CARBON DIOXIDE

C. Barnes,<sup>a</sup> A. Chaffee,<sup>b,c</sup> M.J. Conyngham,<sup>a</sup> B.J. Kennedy<sup>a</sup> and A.F. Masters<sup>a</sup>

a Department of Inorganic Chemistry, University of Sydney, NSW, Australia

b CSIRO Division of Energy Technology, Menai, NSW, Australia

c *present address* BHP Central Research Laboratories, Clayton, Vic., Australia

The catalytic electrochemical reduction of carbon dioxide using organometallic cluster compounds is being investigated. The utility of the clusters was investigated in homogeneous solution, as adsorbants on glassy carbon electrodes, and as components of high surface area carbon electrodes. In each case, the electrochemical responses of the various systems were recorded by cyclic voltammetry under nitrogen and under carbon dioxide.

The organometallic clusters were precipitated onto high surface area carbon which is then pressed and fabricated into a working electrode. The electrochemistry of these high surface area carbon modified electrodes in aqueous solution were compared against similar electrodes fabricated from both nickel and cobalt porphyrinic complexes.

The electrodes fabricated from cluster precursors showed enhanced activity in the electrochemical reduction of carbon dioxide.

## THE EFFECTS OF POTENTIAL POISONS ON THE PERFORMANCE OF NICKEL-BASED OLEFIN OLIGOMERIZATION CATALYSTS

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Department of Inorganic Chemistry, University of Sydney, NSW, Australia.

Highly active olefin oligomerization catalyst systems can be derived from  $[\text{Ni}(\text{R}^2\text{C}(\text{S})\text{C}(\text{R}^1)\text{C}(\text{S})\text{R}^3)(\text{PL}^1\text{L}^2\text{L}^3)\text{X}]$  and appropriate co-catalysts.<sup>1</sup> These are amongst the most active systems reported; some  $6 \times 10^6$  mole of ethylene are oligomerized per mole of catalyst per hour at one atmosphere and 25°C.<sup>2</sup> The successful application of these catalysts is dependant on an evaluation and understanding of the effects of potential poisons on these catalyst systems.

The interactions of these catalysts with CO has been examined spectroscopically. The catalysts are rapidly and completely inhibited by CO; however, removal of the CO restores catalytic activity. A characteristic spectroscopic "fingerprint" is obtained from the poisoned catalyst, and further reaction products of the poisoned catalyst have been identified.

The effects of other potential poisons,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , etc., on the catalyst will also be described.

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## THE ACTIVATION OF ALKANE C-H BONDS

J.K. Beattie, A.F. Masters and M.L. Sparkes

Presented by J.T. Meyers

Department of Inorganic Chemistry, University of Sydney, NSW, Australia.

The activation of C-H bonds in hydrocarbons is a topic of considerable current interest.<sup>1,2</sup> There is considerable incentive to effect this conversion catalytically under mild conditions using readily available reagents. Recently, the stoichiometric conversion of alkanes to alcohols at 50% conversion using palladium acetate was reported.<sup>3</sup>

We report here on the near quantitative conversion of adamantane to 1-adamantanol with 100% selectivity. The reaction can be conducted at approximately 80°C in air.

The reaction can be made catalytic in palladium by an appropriate choice of co-oxidant.

1. *"Selective Hydrocarbon Activation: Principles and Progress"*, J.A. Davies, P.L. Watson, J.F. Liebman and A. Greenberg, Eds., VCH, New York, New York, 1990.
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NOVEL METAL COMPLEXES OF NEW SUBSTITUTED  
PENTAPHENYLCYCLOPENTADIENYL LIGANDS

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Departments of Inorganic and Organic Chemistry, University of Sydney, NSW,  
Australia.

The pentaphenylcyclopentadienyl ligand has the potential of accommodating a variety of substituents both on the  $C_5$ -ring, and on the phenyl rings, to produce a wide range of new ligand types, with different steric and electronic properties.

This work explores in particular substituent control of the steric properties of substituted pentaphenylcyclopentadienyl ligands and the influence of these steric demands on the properties of metal complexes of these ligands.

## COMPLEXES OF THE PENTAPHENYLCYCLOPENTADIENYL ANION

L.D. Field, T.W. Hambley, P.A. Lay, C.M. Lindall and A.F. Masters

Departments of Inorganic and Organic Chemistry, University of Sydney, NSW, Australia.

Precursors to the pentaphenylcyclopentadienyl anion were first reported in 1925<sup>1</sup> and the first metal complex prepared in 1965.<sup>2</sup> Complexes of this ligand exhibit both electronic and structural differences to their complexed cyclopentadienyl and pentamethylcyclopentadienyl analogues. Very few complexes of the pentaphenylcyclopentadienyl anion have been reported.

Reported here are several complexes of iron, ruthenium, molybdenum and chromium utilising the pentaphenylcyclopentadienyl group. It has been found that reaction of the pentaphenylcyclopentadienyl group in either its bromidic, hydridic or anionic form<sup>3</sup> is possible. Reactions are favoured with either substituted or unsubstituted metal carbonyls, in the zero valent state, under rigorously anhydrous conditions. Several coordinating modes are possible - the known  $\eta^5$  mode, and the previously unknown  $\eta^1$ - and  $\eta^6$ - modes.<sup>4</sup> Interconversion between these bonding modes, from the  $\eta^6$ - and  $\eta^1$ - type coordination to the more stable  $\eta^5$ - coordination is observed upon various thermal reactions. Structural and electrochemical studies on selected iron derivatives indicate the per-phenylated cyclopentadienyl ligand exerts a significant effect on the geometry and redox properties respectively, of complexes.<sup>5,6</sup>

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6. L.D. Field, T.W. Hambley, C.M. Lindall and A.F. Masters, *Polyhedron* 1989, 8, 2425.

## NEW DERIVATIVES OF THE PENTAPHENYLCYCLOPENTADIENYL LIGAND

L.D. Field, D.R. Latimer and A.F. Masters

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Australia.

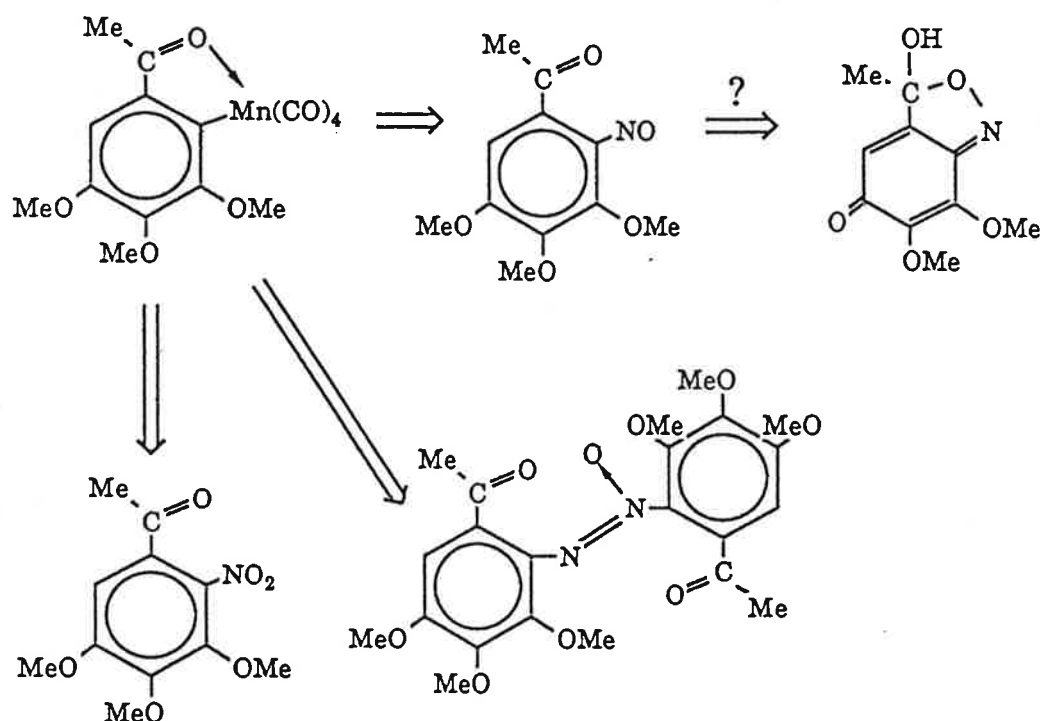
The unique steric and electronic properties of the very bulky pentaphenylcyclopentadiene ligand are being examined. The formation of metal complexes with this ligand has resulted in solubility problems. The synthesis of a ligand precursor incorporating substituents on the phenyl rings has been developed to 'fine-tune' the electronic and solubility properties of the ligand and its complexes. The general synthetic route to substituted pentaphenylcyclopentadiene ligand precursors and the synthesis and characterization of their metal complexes are described.

# THE REACTION OF NITROGEN-CENTRED ELECTROPHILES WITH ORTHOMETALLATED ARYL KETONES

**Meto Leach, Brian Nicholson, Lyndsay Main,**

University of Waikato, Hamilton, New Zealand.

Studies of the reaction of nitronium and nitrosonium ions upon orthomanganated and orthomercurated aryl ketones give a variety of products as summarised below.

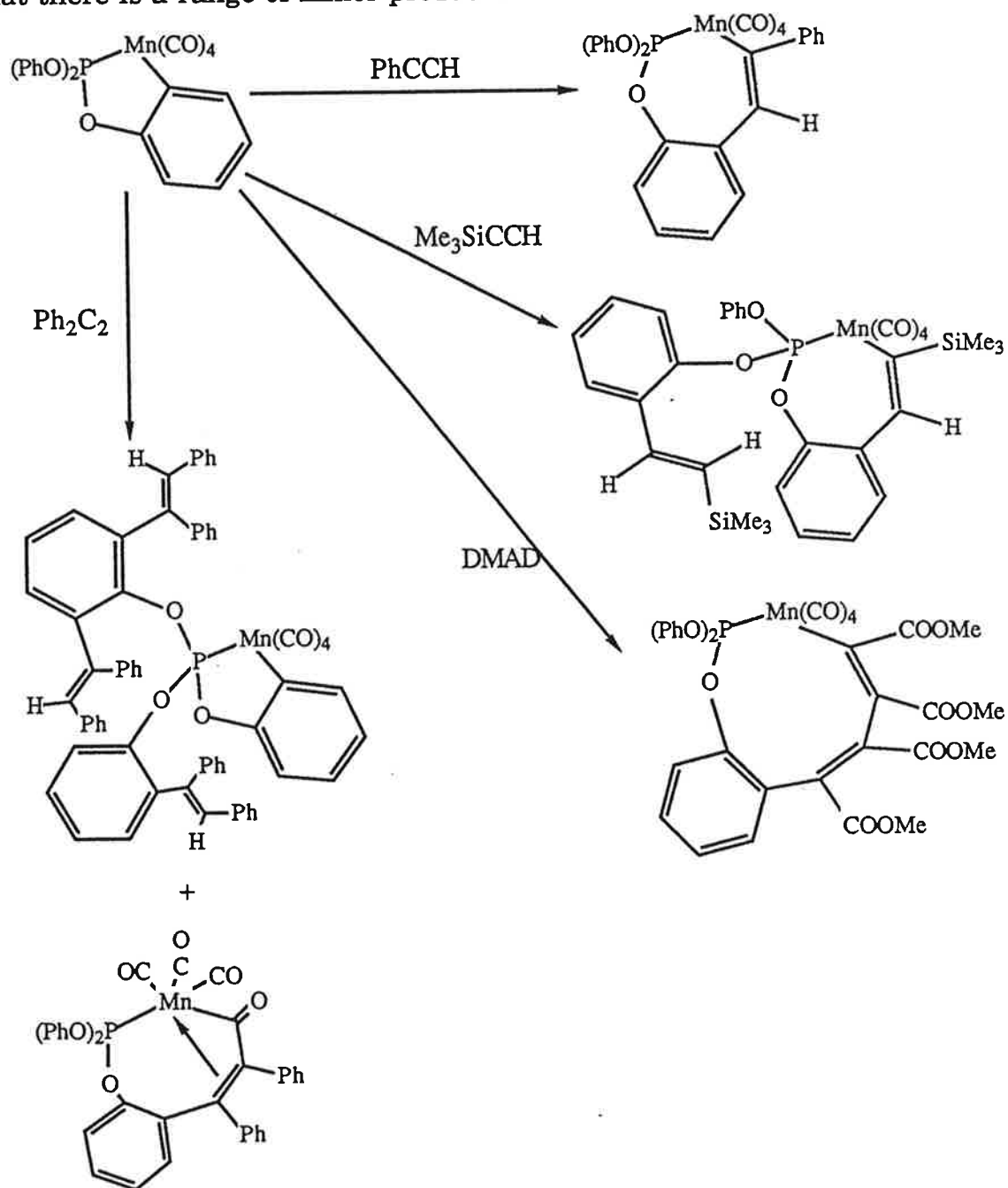


The compound of most interest is the cyclic oxime which is thought to have arisen by electrophilic attack of  $\text{NO}^+$ . Aided by the electron donation ability of the methoxy para to the proposed electrophilic attack, the intermediate then cyclises to form the cyclic oxime. Other nitrogen compounds formed, along with new synthetic routes using orthomanganated and orthomercurated aryl ketones to form the cyclic oxime and nitro compound, will be discussed.

REACTIONS OF  $(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\text{Mn}(\text{CO})_4$  (1) WITH ALKYNESWarren J Grigsby, Brian K Nicholson and Lindsay Main*Chemistry Department, University of Waikato, Hamilton,  
New Zealand*

The photochemical reaction of (1) with  $\text{Ph}_2\text{C}_2$  results in the insertion of the alkyne into the  $\text{Mn}-\text{C}(\text{aryl})$  bond to give a seven membered metallocycle.

Further investigation has shown that the alkyne insertion is regioselective, and that there is a range of minor products.

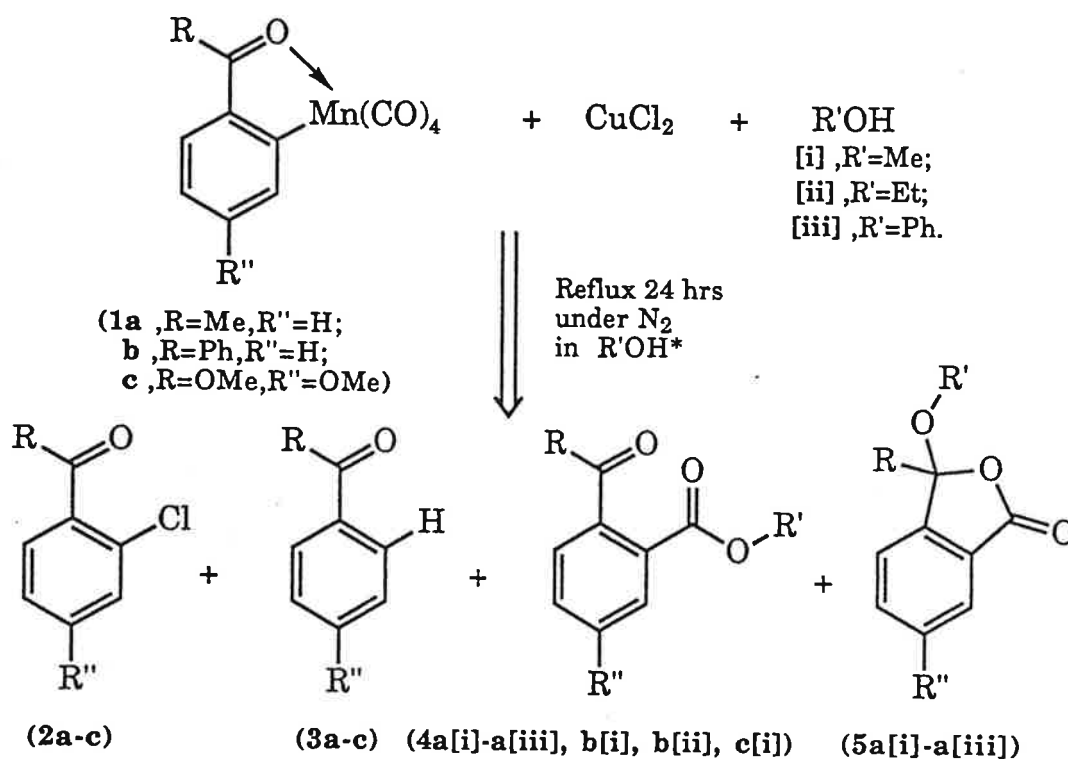




## CLEAVAGE REACTIONS OF *ORTHO*-MANGANATED ACYL ARENES.

**Les Arnold, Lyndsay Main and Brian Nicholson,**  
University of Waikato, Hamilton, New Zealand.

From the reaction between  $\text{RC(O)C}_6\text{H}_4\text{Mn(CO)}_4$ , ( $\text{R}=\text{Me}$ ,  $\text{OMe}$ ,  $\text{Ph}$ ),  $\text{R'OH}$  ( $\text{R}'=\text{Me}$ ,  $\text{Et}$  and  $\text{Ph}$ ) and  $\text{CuCl}_2$  a variety of products can be isolated as summarised below:



\*  $\text{R}' = \text{Ph}$ ; Reflux 96 hrs under  $\text{N}_2$  in THF.

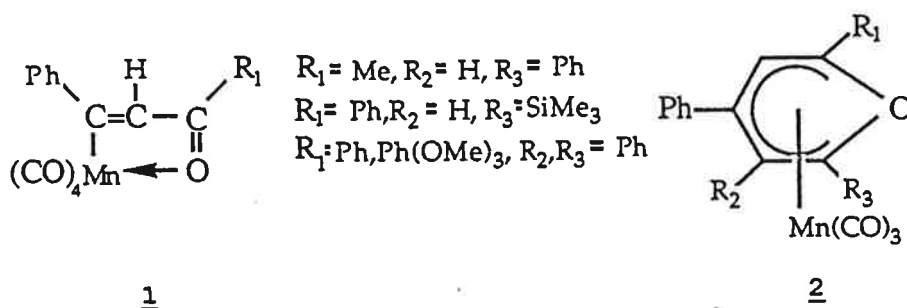
These can be explained in terms of initial  $\text{Mn-C}_{\text{aryl}}$  bond cleavage, or in terms of  $\text{CO}$  insertion into the  $\text{Mn-C}_{\text{aryl}}$  bond, with subsequent attack by the solvent. The manganese is isolated as  $\text{ClMn(CO)}_5$  and  $[\text{ClMn(CO)}_4]_2$ .

The results of reactions of *ortho*-manganated compounds with phosphorus, aluminium and tin chlorides will also be presented.

PREPARATION OF CYCLOMANGANATED ENONESW. Tully, L. Main and B.K. Nicholson

Department of Chemistry, University of Waikato, Hamilton  
(New Zealand).

A general route for the preparation of cyclomanganated enones **1** has been established.



The preparation involves the reaction between the appropriate ketone and benzylpentacarbonylmanganese. Previously reported routes<sup>1</sup> involving carbonyl/alkyne insertion reaction with  $\text{Mn(CO)}_5$  are now surpassed by this direct route involving the use of cheaper starting materials and the readily available benzylpentacarbonylmanganese.

Reactions of the cyclomanganated enones with alkynes,  $\text{Br}_2$ , alkenes and  $\text{HgCl}_2$  will be discussed. From the alkyne reactions pyranyl complexes of the type **2** can be isolated, and subsequent demetallation with  $\text{Ag}^+$  gives pyrylium salts.

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1. B.L. Booth and R.G. Hargreaves, J.Chem.Soc.(A), (1970), 308. see also: P. Deshong, D.R. Sidler, P.J Rybczynski, G.A. Slough and A.L. Rheingold, J.Am.Chem.Soc. 110 (1988) 2575

RAMAN SPECTROSCOPIC STUDY OF  
RUTHENIUM TRIS-BIPYRIDYL PHOTOSENSITISER  
BOUND TO COLLOIDAL TITANIUM DIOXIDE  
SEMICONDUCTOR.

Anthony M. Cartner and Gary Brightwell  
Chemistry Department  
University of Waikato

The pH-dependence of the adsorption of the photosensitiser onto the titania colloid has been examined using a membrane filtration technique. Results indicate that the binding is specific rather than contact. Resonance Raman and laser fluorescence spectra of bound and unbound photosensitiser will be discussed in terms of the excited state species formed on excitation into the absorption envelope of the molecular ion and of the efficiency of electron injection into the valence band of the semiconducting colloid.

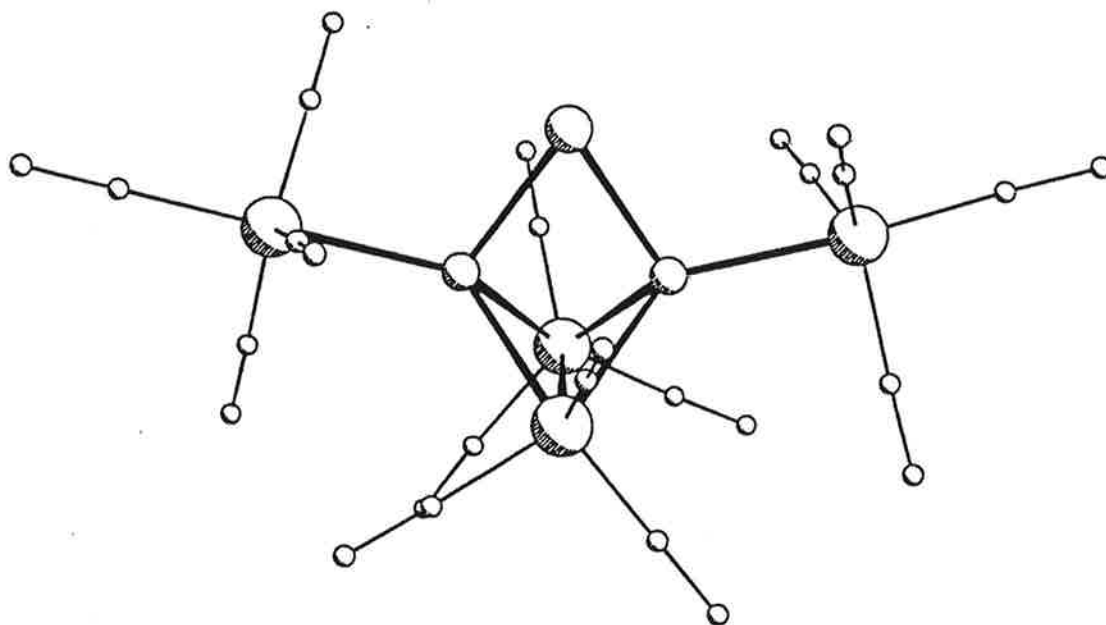


# SYNTHESIS OF A NEW COBALT CARBONYL CLUSTER WHICH INCORPORATES A Si-S-Si BRIDGE

M.L. Van Tiel, K.M. Mackay and B.K. Nicholson,  
Chemistry Department, University of Waikato.

The reaction of  $\text{H}_3\text{SiSSiH}_3$  with  $\text{Co}_2(\text{CO})_8$  at room temperature gives the Si-S-Si bridged cobalt carbonyl cluster  $\text{SSi}_2\text{Co}_4(\text{CO})_{14}$ . This cluster forms yellow/orange diamond shaped crystals from toluene in 20 to 30% yields along with the square bipyramid cluster  $\text{S}_2\text{Co}_4(\text{CO})_{10}$ .

X-ray crystal structure of the orthorhombic cluster revealed a new bonding arrangement consisting of a Co-Co bond with two bridging  $\text{SiCo}(\text{CO})_4$  groups which are linked by a sulphur atom. The Co-Co distance of  $2.622(1)\text{\AA}$  is markedly longer compared to that for  $\text{Co}_2(\text{CO})_8$   $2.52\text{\AA}$  and  $\text{Si}(\text{Co}_2(\text{CO})_7)_2$  at  $2.528\text{\AA}$ . The Si-Co terminal distance ( $2.298(3)\text{\AA}$ ) is similar to that found for other clusters (eg  $(\text{CO})_4\text{CoSiCo}_3(\text{CO})_9$  at  $2.288\text{\AA}$ ), but the Si-Co distances to the central Co-Co bond (ave  $2.301(10)\text{\AA}$ ) are slightly longer compared to similar small clusters. The Si-S-Si bridging unit shows a very acute angle of  $70.3(1)^\circ$  with Si-S distance of  $2.171(3)\text{\AA}$ .



A similar reaction using  $\text{H}_3\text{SiOSiH}_3$  with  $\text{Co}_2(\text{CO})_8$  has been investigated and shows no formation of an analogous product.

## Chromate Encapsulation by Zeolite Y

**M.L. Brown** and A.G. Langdon.

University of Waikato, Hamilton, New Zealand.

Sodium chromate has been encapsulated within the structure of Y type zeolite by firing zeolite/sodium chromate mixtures. Under optimum conditions up to 2% chromate by weight was irreversibly bound to the zeolite with minimal lattice degradation, shown by powder X-ray diffraction and B.E.T surface area studies. The encapsulated chromium species was characterised by Laser Raman and ESR spectroscopies. Raman spectra indicated discrete chromate oxyanions. Controlled reduction of chromate zeolite by hydrogen gas at elevated temperatures resulted in the appearance of an anisotropic ESR signal,  $g_{||} = 1.979$  and  $g_{\perp} = 1.919$ , which was assigned to an axially symmetric Cr(V) species. The stoichiometry of chromate encapsulation, the site of reaction and a structure for the resulting chromate lattice species have been proposed and will be discussed .

Electroacoustic Studies of Suspensions of  
Metal Oxides

*Michael James, Richard W. O'Brien, Robert J. Hunter and  
James K. Beattie*

*School of Chemistry, University of Sydney,  
Sydney, New South Wales 2006, Australia.*

Electroacoustics describes the interaction of ultrasound with charged species in solution. Debye described the ionic vibration potential which is the alternating electric field generated when a sound wave passes through an ionic solution. A much larger effect is the colloid vibration potential which arises from the inertial difference between a charged colloidal particle and its ionic atmosphere. The converse electrosonic amplitude is the sound wave generated when an alternating electric field is applied to a colloidal suspension.

Sound of frequency 100 KHz to 10 MHz interacts strongly with particles of 1.0 to 0.1  $\mu$ . A new scientific instrument is under development in Sydney which exploits this effect. It enables the measurement of the charge on colloidal particles (the zeta potential) in opaque colloidal suspensions. Current methods such as electrophoresis and light scattering require very dilute suspensions. Electroacoustics allows measurements on suspensions of 1-10 volume per cent which represent practical concentrations.

Measurements on suspensions of alumina will be described. Good agreement is found between electroacoustic and electrophoretic measurements of both the zeta potential and the isoelectric point if the correct mass average of the particle size distribution is used.

## EMISSION SPECTROSCOPY OF CHROMIUM DOPED ALUMS

R. S. Armstrong, A. J. Berry, B. D. Cole, and K. W. Nugent.Department of Inorganic Chemistry, The University of Sydney,  
Sydney, NSW, 2006, AUSTRALIA.

Alums have the general formula  $M^I M^{III} (XO_4)_2 \cdot 12H_2O$ , (X is either S or Se), and occur in two main structural forms known as  $\alpha$  and  $\beta$ . An electronic emission is observed in low temperature (4.2 K), single crystal studies of chromium alums. As a consequence of the high emission intensity it is possible to record the luminescence spectrum of the chromium species doped into other alum structures.

In experiments such as absorption and epr spectroscopy where dilution of the species of interest is often necessary, spectra are obtained by doping the species under investigation into a host lattice. In the interpretation of these results, it is generally assumed that the lattice has little effect upon the impurity. The observed properties, however, will be subject to the constraints imposed by the lattice on the dopant molecule. The nature and magnitude of these effects usually can not be determined. For a series of chromium doped alums, the influence of the lattice can be investigated through variations in the emission spectrum.

The antisymmetric stretching mode of  $[Cr(H_2O)_6]^{3+}$ ,  $\nu_3$ , is used to investigate site size effects. The vibrational energy can only be determined because of vibronic coupling to the electronic emission. Normal vibrational spectroscopy is unable to distinguish the energy of a doped species from the similar, and much more intense, host lattice signal.

Variations in the energy and splitting of the electronic origin are attributed to the effect of  $\pi$  overlap involved in water coordination to chromium. Differences in the extent of oxygen lone pair and chromium  $t_{2g}$  orbital overlap are reflected in the electronic origin energy, in accordance with the nephelauxetic effect. The origin splitting derives from spin-orbit coupling in a trigonal field. The hydrogen bonding network of the alum lattice distorts the  $[Cr(H_2O)_6]^{3+}$  cation, generating trigonal symmetry. The trigonality is transmitted to the metal orbitals through the  $\pi$  overlap, and it can be shown that the spin-orbit splitting is proportional to the extent of  $\pi$  bonding.

## INFRARED AND RAMAN SPECTRA OF

 $(\eta^6\text{-arene})\text{M}(\text{CO})_3$  COMPLEXES(M = Cr, Mo or W, and arene =  $\text{C}_6\text{H}_6$ , 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$  or  $\text{C}_6\text{Me}_6$ )

- AN INSIGHT INTO METAL-ARENE BONDING.

*R.S.Armstrong, M.J.Aroney, C.M.Barnes and K.W.Nugent.**Department of Inorganic Chemistry, University of Sydney,  
Sydney, New South Wales 2006, Australia.*

A vibrational spectroscopic study of  $(\eta^6\text{-arene})\text{M}(\text{CO})_3$  complexes (M = chromium, molybdenum or tungsten; arene = benzene, mesitylene or hexamethylbenzene) has been carried out. The infrared spectra were obtained in the solid and solution states; the Raman spectra in the solution state only. From the results, most of the fundamental vibrations have been assigned over the region  $100\text{--}3100\text{cm}^{-1}$ . The relative band intensities (both infrared and Raman) for the metal-arene, metal-carbon (M-CO), and carbonyl vibrational modes have been determined. The infrared and Raman intensities are related, respectively, to the polarities and polarizabilities of the individual bonds within the molecular systems studied. Variations in these bond properties were examined by analyzing the trends in the frequencies and intensities of the above vibrational modes with change in the metal or the arene in  $(\eta^6\text{-arene})\text{M}(\text{CO})_3$ . The results are interpreted to indicate the relative importance of  $\pi$ -donation from the arene to the metal and of  $\delta$ -backbonding. A molecular orbital scheme is proposed which accounts for the changes observed in the degree of  $\pi$ - and  $\delta$ -bonding within the group of complexes studied. The variation of arene ligand modes, such as the carbon-carbon stretch or ring breathing mode, have also been examined in order to determine if there is any change in the aromaticity of the arene upon complexation to the metal tricarbonyl moiety.

SYNTHESIS AND CHARACTERIZATIONS OF LANTHANIDE(III) COMPLEXES OF  
TETRAPYRIDYLPORPHINE

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University of Zimbabwe, PO Box MP 167  
Mt. Pleasant, Harare, ZIMBABWE

ABSTRACT

Organic solvent- and water-soluble lanthanide(III) complexes of  $\alpha$ ,  $\beta$ ,  $\tau$ ,  $\delta$ -tetra(4-pyridyl) porphine with general formula  $\text{Ln}^{\text{III}}\text{TPyP}$ , stable in neutral and highly basic solutions have been synthesised for Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. The complexes were purified using column chromatography, with basic alumina as the stationary phase and then recrystallised from hot methanolic solutions. Characterizations were carried out using microanalytical, UV-visible and H-NMR techniques. The UV-visible spectra confirmed the presence of the lanthanide ion in the porphyrin moiety by the complete disappearance of the four visible absorption bands of the free base TPyP and the appearances of bands characteristics of the metalloporphyrins. Well-resolved H-NMR spectra were observed for the TPyP protons of Yb(III), Tm(III) and Er(III) complexes in DMSO- $d_6$  solution. The phenyl proton resonance shifts are downfield and are consistent with a dominant dipolar interaction with the metal ion situated significantly out of the porphyrin plane.



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Ralph	Thomson	University of Waikato	
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