XXVII INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY

ABSTRACTS

PART 1

Conference details
Plenary and SessionLectures

BROADBEACH, QUEENSLAND, AUSTRALIA

2-7 JULY, 1989

XXVII INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY

ABSTRACTS

Broadbeach, Queensland
Australia

2 - 7 July, 1989

XXVII INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY

Scientific Program

The contributions to XXVII ICCC are in the form of Plenary Lectures (coded **P**), Session Lectures (coded **S**) and Posters.

An **Author Index** is placed at the end of this Book of Abstracts. The Presenting Author of a paper is asterisked.

Authors are solely responsible for the content, style and quality of their Abstracts, which were reproduced directly from the originals.

The Abstracts are numbered consecutively; the timetable for the presentation of the Plenary and Section Lectures is listed in the Conference Handbook.

The Posters are coded **M**, **W** or **T** according to whether they are scheduled for display in the Monday, Wednesday or Thursday Session. The number allocated to the Poster corresponds to the number of the Poster Board on which it will be displayed in the Poster Room. A plan of the numbering system for the boards will be posted on the Notice Board adjacent to the Service Desk in the Poster Room.

In addition to the formal Session on the days indicated, the posters will also be available for viewing during lecture sessions, during the refreshment and meal breaks and on Monday and Wednesday evening until 2000 (8pm). **It is important that exhibitors conform to the schedule for the erection and the removal of posters, as indicated below.**

Poster presenters are requested to place their photograph prominently on their display and to leave a space for affixing messages from interested delegates. The same number card will be used for the three separate sessions and should be left on the board when the poster is removed.

Monday Poster Session (M)

Setting up	Monday morning from 0800
Formal display	Monday from 1530-1730
Author attendance	Monday 1530-1630
Removal	Before 0800 Wednesday, but POSTERS SHOULD PREFERABLY BE AVAILABLE FOR VIEWING ON TUESDAY MORNING.

Wednesday Poster Session (W)

Setting up	Wednesday morning from 0800
Formal display	Wednesday from 1530-1730
Author attendance	Wednesday 1530-1630
Removal	Before 0800 Thursday, but POSTERS SHOULD PREFERABLY BE AVAILABLE FOR VIEWING UNTIL 1800 ON WEDNESDAY EVENING.

Thursday Poster Session (T)

Setting up	Thursday morning from 0800
Formal display	Thursday from 1500-1800
Author attendance	Thursday 1530-1630
Removal	Before Friday 1200

A number of Microsymposia, (coded MS and listed below), will be held in conjunction with the Poster Sessions. They are scheduled into the second hour of the formal Poster Sessions on Monday, Wednesday and Thursday. The Organising Committee has invited some delegates, whose Posters fall into these subject areas, to make a short oral presentation on their work. The papers which will be so presented are indicated, both below and on the Abstract.

Other Posters with direct relevance to the theme of a Microsymposium are indicated.

MICROSYMPOSIA

Monday

MS1 SPECTROSCOPY AND PHOTOCHEMISTRY OF COORDINATION COMPLEXES

Invited Oral Presentation:	M1 - M7
Associated Papers:	M8 - M32

MS2 BIOINORGANIC CHEMISTRY OF VANADIUM, MOLYBDENUM AND MANGANESE

Invited Oral Presentation:	M60 - M66
Associated Papers:	M67 - M75

MS3 METAL CLUSTERS

Invited Oral Presentation:	M33 - M38
Associated Papers:	M39 - M59

Wednesday

MS4 ELECTRONIC PROPERTIES OF INORGANIC SOLIDS

Invited Oral Presentation:	W1 - W5
Associated Papers:	W6 - W9

MS5 BIOCHEMISTRY OF IRON AND COPPER

Invited Oral Presentation:	W10 -W16
Associated Papers:	W17 - W33

MS6 ELECTRON TRANSFER AND ELECTROCHEMISTRY

Invited Oral Presentation:	W34 - W39
Associated Papers:	W40 - W58

Thursday

MS7 BIOINORGANIC CHEMISTRY OF PLATINUM COMPLEXES

Invited Oral Presentation: T1- T6

Associated Papers: T7 - T10

MS8 BOND ACTIVATION BY METAL COMPLEXES AND RELATED CATALYSIS

Invited Oral Presentation: T30 - T36

Associated Papers: T37 - T53

MS9 CHIRAL COMPLEXES

Invited Oral Presentation: T64 - T69

Associated Papers: T70 - T81

PLENARY

LECTURES

INTRAMOLECULAR CONTROL OF EXCITED STATE ELECTRON TRANSFER

Thomas J. Meyer

Department of Chemistry, University of North Carolina, Chapel Hill, NC

Metal to ligand charge transfer (MLCT) excited states of polypyridyl complexes of Ru(II), Os(II), and Re(I) undergo well defined excited state electron transfer processes. Studies in solution have shown that rapid, efficient, electron transfer of excited states such as $[Ru(bpy)_3]^{2+*}$ bpy is 2,2'-bipyridine can occur and the details of these reactions can be accounted for by using contemporary theories of electron transfer. We have been exploring the preparation of complex chemical systems which contain combinations of MLCT light absorbers and quenchers in the same molecular unit. The goal is to learn how to control intramolecular electron and energy transfer processes following excitation at the MLCT chromophore.

In this work, we have utilized derivatized polypyridyl complexes of Ru(II), Os(II), and Re(I). In chromophore quencher complexes we have demonstrated that following MLCT excitation, rapid efficient intramolecular electron transfer can occur either to electron acceptors such as pyridiniums or from electron donors such as phenothiazines. In modified complexes which contain both electron transfer donors and acceptors, light induced redox splitting can be made to occur to give transient redox separated states in which the initial excited state energy is converted into spatially separated oxidative and reductive equivalents. In ligand bridged complexes, either energy or electron transfer can be induced across the ligand bridge. In these complexes, the initial distribution of the excited electron between possible acceptor sites can be dictated in some cases by substituent effects on the polypyridyl ligands and by the nature of the bridging ligand. A series of experiments has also been carried out on soluble polymers. In these experiments combinations of light absorbers and quenchers have been chemically attached to a 1:1 styrene-chloromethylstyrene copolymer. It has been possible to show that electron and energy transfer shuttles can be set up following excitation of a polymer bound MLCT chromophore. In more complex polymers containing both quenchers and chromophores, we have been able to demonstrate that long range energy transfer can occur through anthryl groups by an energy transfer cascade mechanism. It had also been possible to demonstrate that multiple redox equivalents can be created and stored in polymers that contain multiple chromophores.

P2

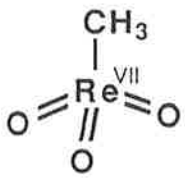
ORGANOMETALLIC OXIDES - A BORDERLINE CLASS OF COMPOUNDS BETWEEN INORGANIC AND ORGANOMETALLIC CHEMISTRY: SYNTHETIC, STRUCTURAL, AND CATALYTIC ASPECTS

Wolfgang A. Herrmann

Anorganisch-chemisches Institut der Technischen Universität München, Garching bei München (Germany)

During the past decades, organometallic chemistry has been most active and successful in the exploration of the syntheses, structures, reactivity, and catalytic applications of low-valent transition metal compounds.[1] Much less is known, however, about compounds containing metals in high oxidation states. Oxidation processes, the most important type of industrially applied reactions, are dependent on catalysts of this type.

This plenary lecture will utilize examples containing the elements rhenium, technetium, and osmium to illustrate some basic features of high-valent organometallic compounds, and will focus on their preparation, structural peculiarities, reactivity, and catalysis. The key compounds 1 - 3 will be discussed in detail. Most of the reported results are as yet unpublished.



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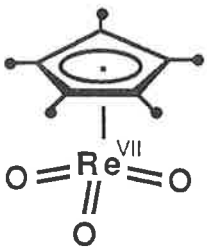

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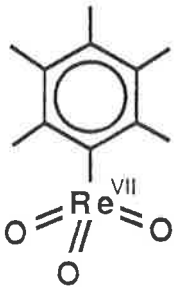

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[1] W. A. Herrmann, Comments Inorg. Chem., 1985, 7, 73.

TRANSITION METAL THIOLATES: SYNTHETIC, CATALYTIC AND BIOMIMETIC ASPECTS.

A. Nakamura, N. Ueyama, and K. Tatsumi

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, JAPAN

The following mono- and dithiolates are synthesized by ligand substitution or exchange in organic solvents.

a) Tris-chelates of Nb(V) and Ta(V) with 1,2-ethanedithiolato and related ligands.
b) Mono(pentamethylcyclopentadienyl)bis(dithiolato) complexes of Ta(V), $[Cp^*Ta(S\frown S)_2]$.
c) Arenethiolato and areneselenolato complexes of Mn(II), Fe(II), Mo(V) etc with or without bulky ortho-substituents.
d) Oligopeptide thiolate complexes of Ag(I), Fe(II), Mn(II), and Mo(V) as models of metalloenzymes.
e) Chelating peptide oligothiolato complexes of Fe_2S_2 and Fe_4S_4 cores as models of iron-sulfur proteins.

X-ray structures, spectroscopic features, redox behaviours and reactivities of these new complexes will be presented. Some of these catalyze dithiol condensation, air oxidation of alcohols, and ring opening polymerization of alkylene sulfides.

The reaction of $Cp^*Ta(SCH_2CH_2S)_2$ with Li_2S_2 in THF gave a novel anionic tri(sulfido) tantalum(V) complex $\{Li_2[Cp^*TaS_3]\}_2$ with a hexagonal prizmatic $Ta_2Li_4S_6$ core which serves as a starting material for other polynuclear bridging sulfido complexes. Similar ligand exchange reaction of $[Ta(SCH_2CH_2S)_3]^-$ anion with $HOCH_2CH_2SH$ or $HOCH_2CH_2OH$ readily gave tris-chelates of the dianions of these ligands.

The peptide thiolate complexes are found to have their solution structures quite similar to the metal sites of native proteins when the peptide ligands simulate the peptide sequences near the metal. Coupled with the redox behavior and the catalysis, the thiolato complexes are important in biomimetic aspects.

P4

TARGETING DNA SITES WITH SIMPLE METAL COMPLEXES

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Transition metal complexes have been designed which recognize and react at specific sites along the DNA strand. The complexes, mainly derivatives of tris(phenanthroline) metal cations, possess several features in common which are critical to their application as site-specific DNA binding molecules. The complexes all are rigid, chiral, and contain a coordinatively saturated metal ion at their core [1].

Most of the complexes to be described target DNA sites based upon shape-selective interactions, where the complexes are matched in terms of shape and symmetry to local conformations along the DNA strand. Considerations of shape have led to the development of both complexes which recognize the shallow minor groove surfaces of A-form helices and complexes which bind preferentially to open major groove sites. $Ru(TMP)_3^{2+}$, our probe for the A-conformation, binds avidly to A-form polynucleotides and in the presence of light promotes cleavage of the DNA in a reaction mediated by singlet oxygen [2]. A new class of rhodium(III) coordination complexes , the intercalating 9,10-phenanthrenequinonediimine (phi) complexes $Rh(phen)_2(phi)^{3+}$ and $Rh(phi)_2(bpy)^{3+}$ efficiently cleave supercoiled and linear DNA at high nucleotide/Rh ratios upon irradiation at long wavelengths (310-360 nm) [3]. $Rh(phi)_2bpy^{3+}$, owing to its efficiency and low selectivity in cleavage, is likely to be extremely useful as a protein photo-footprinting reagent. $Rh(phen)_2phi^{3+}$, which may bind intercalatively only at opened major groove sites because of steric constraints of the ancillary ligands, provides a powerful companion for the A-form probe $Ru(TMP)_3^{2+}$. This pair can serve as a unique tool to map DNA contours, in other words, to map specifically and in detail the local variations in secondary structure along helices. But perhaps the most striking illustration of *shape selection* is given by the remarkably specific cleavage of DNA sites by $Rh(DIP)_3^{3+}$[4]. This complex binds to and, upon photoactivation, cleaves both DNA strands near the base of a DNA cruciform with remarkably high specificity, and therefore serves as a site-specific probe of DNA tertiary structure.

Features of hydrogen bonding may also be considered in constructing transition metal complexes which recognize specific DNA sites. In particular, a family of simple metal complexes containing amino acids and peptides as coordinated ligands have been synthesized and the binding of these complexes to DNA will be described and compared with those which recognize DNA on the basis of shape-selection. Both in terms of their structure and their basis for targeting DNA sites, simple transition metal complexes may provide useful models to explore those principles important to the recognition of DNA sites by DNA regulatory proteins.

1. J.K. Barton, *Science*, **1986**, *233*, 727.
2. H.Y. Mei and J. K. Barton, *Proc. Natl. Acad. USA* **1988**, *85*, 1339 .
3. A. M. Pyle, E. Long, and J.K. Barton, **1989** submitted for publication .
4. M.R. Kirshenbaum, R. Tribolet, and J.K. Barton, *Nucleic Acids Res.* **1988**, *16*, 7943.

CARBENES, CARBIDES AND CARBON: TRANSFORMATIONS OF ALKYNES AT METAL CENTRES

Michael I. Bruce

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University of Adelaide, South Australia 5001

(Burrows Lecture)

Over the last ten years, much of our work has involved studies of novel transformations of alkynes on mono- and poly-nuclear metal centres with up to five metal atoms. The lecture will summarise earlier results which lead to the development of the chemistry of transition metal-substituted alkynes (metal acetylides), of vinylidene complexes, and of a variety of derivatives obtained by cycloaddition reactions.

More recent investigations to be described include:

(i) new alkyne oligomerisation reactions affording tri-, tetra- and pentamers;

(ii) conversion of alkynes to carbides;

(iii) novel coupling reactions of C_2 molecules with unsaturated hydrocarbons on metal clusters.

P6

INTERLACING MOLECULAR THREADS ON TRANSITION METALS

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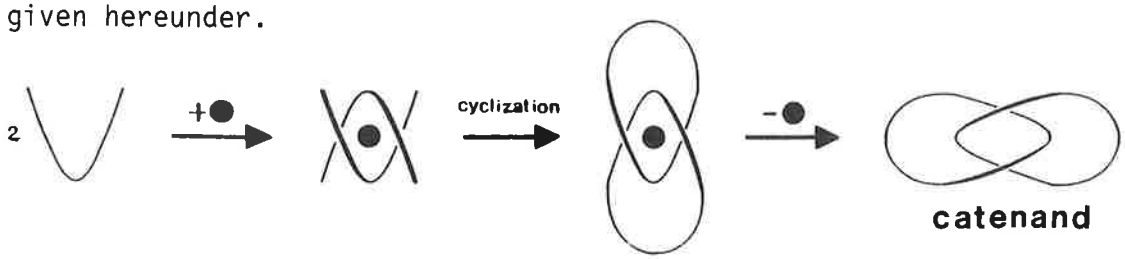
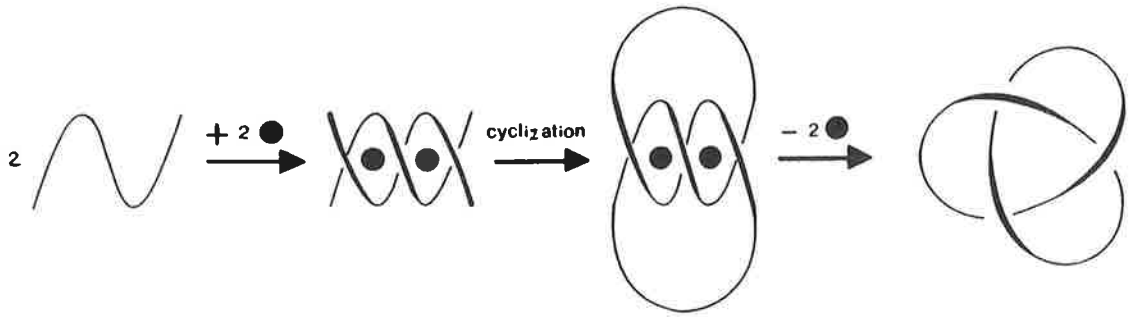
Making topologically novel molecules like catenanes (interlocked rings) and knots has been a challenge in Chemistry for decades.

Transition metals are powerful tools in this view since they are able to bind and collect two or more coordinating molecular threads and, by further reactions, the precursor complex obtained can lead to interlaced systems. This new type of three-dimensionnal template effect has been developed in our group for a few years. The general principle is given hereunder.





The first strategy has allowed the synthesis of catenates (complexes) and catenands (free ligands containing interlocked macrocycles) [1]. The most representative example is that of the copper (I) catenate, the ligand consisting of two interlocked 30-membered rings. The particular topology of the catenands and the topography of the corresponding complexes are responsible for the very special electrochemical, photophysical and kinetic properties of the catenates.

Recently, a synthetic molecular trefoil knot could be made [2].

1. C.O. Dietrich-Buchecker and J.P. Sauvage, Chem. Rev., 1987, **87**, 795 and references.
2. C.O. Dietrich-Buchecker and J.P. Sauvage, Angew. Chem., 1989.

SESSION

LECTURES

DYNAMICS OF REACTIVE INTERMEDIATES AS PROBED BY PHOTOCHEMICAL TECHNIQUES

Peter C. Ford

Department of Chemistry, University of California
Santa Barbara, California 93106 USA

Thermal reaction cycles, e.g., those responsible for homogeneous catalysis, often proceed via high energy intermediates which can only be inferred from kinetics, stereochemistry or intuition. It is sometimes possible to generate the same species as the primary product of a photochemical reaction and to interrogate the spectra and dynamics of such intermediates directly by flash photolysis. Described is an example drawn from recent studies.

Flash photolysis of the Rh(I) complexes trans-$RhCl(CO)L_2$ (L = PMe_3 or $Ptol_3$) in benzene gives in each case the "tricoordinate" intermediate $RhClL_2$ (A) which undergoes first order reaction to form a bleached transient (B) believed to be the phenyl hydride adduct (eq. 1)[1,2]. This contrasts to the behavior of the intermediate from photolysis of trans-$RhCl(CO)(PPh_3)_2$ for which competitive second order trapping by CO and dimerization (eq. 2) were shown to dominate [3]. The intermediate A for L = PMe_3 proved to be an order of magnitude more reactive with benzene than for L = $Ptol_3$ and gave a much longer lived bleached transient. In cyclohexane only the intermediate from the PMe_3 complex underwent analogous C-H activation of the solvent. The bleached transients are proposed to be intermediates in the photocatalytic carbonylations of hydrocarbons reported by others [4] for such Rh(I) complexes. Discussed will be studies mapping the sequence of events indicated by eq. 1.

$$(1)\quad RhCl(CO)L_2 \xrightarrow[-CO]{h\nu} \underset{A}{RhClL_2} \xrightarrow{k_a} \underset{B}{\overset{R}{\underset{H}{RhClL_2}}} \xrightarrow[+CO]{k_b} RhCl(CO)L_2$$

$$(2)\quad A \xrightarrow{k_{co}[CO]} \text{trans-}RhCl(CO)L_2$$
$$A \longrightarrow 1/2\ [RhClL_2]_2$$

These studies were supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy and by the U.S. National Science Foundation.

[1] C. T. Spillett and P. C. Ford, J. Am. Chem Soc. 1989, 111, xxxx
[2] T. L. Netzel (Amoco Research Corp.) to be submitted.
[3] Wink, D. A.; Ford, P. C. J. Amer. Chem. Soc. 1987, 109, 436-442
[4] a) Kunin, A. J.; Eisenberg, R.; J. Amer. Chem. Soc. 1986, 108, 535-6
b) Sakakura, T.; Tanaka, M. Chem. Let. 1987, 249-52; 1113-6; JCS Chem. Comm. 1987, 758-9

S2

Photochemical Water Exchange in Chromium(III) Complexes and Mechanism of Solvent Assisted Excited State Deactivation.

O. Mønsted.

Department of Inorganic Chemistry.
University of Copenhagen. Denmark.

The very limited data on photochemical water exchange in photochemically active aquametal ions has been supplemented by oxygen-18 labelling studies of photoinduced water exchange in a number of amineaquachromium(III) complexes including all the possible ammineaquachromium(III) complexes and a selected number of complexes coordinated with chelate diamines. Exchange of coordinated water is found to dominate over aquation of the amine ligand, and for a significant number of the complexes studied this is contrary to predictions from widely accepted empirical and semiempirical models.

Product distributions are best accounted for by an associative interchange mechanism and *trans* attack of the entering water molecule, and for such a transition state, ligand field considerations predict that the lowest excited quartet state is of comparable energy to the quartet ground state and lower in energy than the lowest doublet excited state. This suggests that the solvent assisted deactivation process of both the excited doublet and quartet states occurs via a quartet excited transition state.

This mechanism will be further elaborated in relation to data for thermal reactivities and photochemical data for other metal centers.

References:

L. Mønsted and O. Mønsted: Coord. Chem. Rev. Accepted for publication, and

L. Mønsted and O. Mønsted: Acta Chem. Scand. A40 (1986) 637.

SUPRAMOLECULAR PHOTOCHEMISTRY

Vincenzo Balzani
"G. Ciamician" Department of Chemistry of the University and F.R.A.E. - C.N.R. Institute, Bologna, Italy.

In the field of photochemistry, which is at the crossroads of chemistry, physics and biology and at the interface between matter and light, the quantitative growth of the last 20 years has been accompanied by profound qualitative changes. The interest of the research workers has progressively moved from photoreactions taking place inside molecules (intramolecular photochemistry)[1] to processes taking place between long-lived excited states and suitable reaction partners (intermolecular electron and energy transfer processes)[2]. In the last few years a trend to study artificial assemblies of two or more molecular components (supramolecular photochemistry) has also emerged with the dual aim of making progress toward the understanding of photobiological processes and the design of artificial systems capable of performing useful functions [3].

In the area of supramolecular photochemistry one can distinguish systems made by (i) covalently linked molecular building blocks (e.g., dyads, triads, tetrads, polynuclear complexes) [4] and (ii) molecular entities associated by electrostatic interaction, hydrogen bonds, or other intermolecular forces (host-guest systems, ion-pair species, second-sphere coordination complexes). [5]

Several examples of both systems will be illustrated and discussed, with particular emphasis on complexes of Ru(II), Eu(III), and Pt(II).

1 - V. Balzani and V. Carassiti, "**Photochemistry of Coordination Compounds**", Academic Press, London, **1970**.

2 - V. Balzani, F. Bolletta, M.T. Gandolfi and, M.F. Manfrin, **Top. Curr. Chem.**, **1978**, 75, 1.

3 - V. Balzani, ed. : "**Supramolecular Photochemistry**", Reidel, Dordrecht, **1987**.

4 - See, e. g. , C. A. Bignozzi, C. Paradisi, S. Roffia, and F. Scandola, **Inorg. Chem.**, **1988**, 27, 408.

5 - See, e.g., R. Ballardini, M.T. Gandolfi, V. Balzani, F.H. Kohnke, and J.F. Stoddart, **Angew. Chem. Int. Ed. Engl. 1988**, 27, 692.

S4

COMPOUNDS WITH RUTHENIUM-SILICON AND OSMIUM-SILICON BONDS

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

Department of Chemistry, University of Auckland, Auckland, New Zealand

Several recent reports have described base-coordinated transition metal silylene complexes. The work to be reported here has as its goals (1) the characterization of silylene complexes without base-stabilization and (2) an examination of the reaction possibilities associated with a transition metal-bound silylene. The approach is to prepare both coordinatively saturated and unsaturated complexes, $L_nM\text{-}SiR_2X$, where X is SiR_3, alkyl, aryl, H, halide and to explore the potential of the various X-functions as leaving-groups or migrating-groups. The synthesis of $L_nM\text{-}SiR_2X$ has been achieved by using either silanes or mercury-silicon compounds such as $Hg(SiMe_3)_2$.

Reaction between $MPhCl(CO)(PPh_3)_2$ (M = Ru or Os) and silanes, R_3SiH, results in elimination of C_6H_6 and formation of $M(SiR_3)Cl(CO)(PPh_3)_2$. In this way $Ru(SiEt_3)Cl(CO)(PPh_3)_2$, $Ru(SiCl_3)Cl(CO)(PPh_3)_2$, and $Os(SiCl_3)Cl(CO)(PPh_3)_2$ have been prepared. The $SiCl_3$-ligand can be substituted at Si without rupture of the metal-Si bond and compounds derived include $Ru[Si(OEt)_3]Cl(CO)(PPh_3)_2$ and $Os(SiMe_3)Cl(CO)(PPh_3)_2$. The five coordinate compounds are all coloured and X-ray crystal structure determinations of $Ru(SiEt_3)Cl(CO)(PPh_3)_2$, $Ru[Si(OEt)_3]Cl(CO))(PPh_3)_2$ and $Os(SiMe_3)Cl(CO)(PPh_3)_2$ reveal an approx. square pyramidal geometry with the Si-ligand apical and the triphenylphosphine ligands arranged trans. Structural details will be presented and discussed.

Reaction between $Hg(SiMe_3)_2$ and $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ follows an unusual course in that CO is lost and C_2H_4 retained in the product, $Os(SiMe_3)(HgSiMe_3)(C_2H_4)(CO)(PPh_3)_2$. This complex is also unusual in having cis triphenylphosphine ligands. Reaction between $Hg(SiMe_3)_2$ and $OsHCl(CO)(PPh_3)_3$ produces a mixture of products one of which is $Os(SiMe_3)Cl(CO)(PPh_3)_2$. Another is $Os(SiMe_2C_6H_4PPh_2)(C_6H_4PPh_2)(CO)(PPh_3)$. The detailed structure of this compound will be described and a possible mechanism for its formation will be presented.

THE COORDINATION CHEMISTRY OF SOME MULTIPLY-BONDED MAIN-GROUP COMPOUNDS

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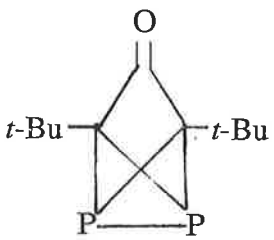
Phosphaalkynes, RC≡P, exhibit a highly varied coordination chemistry. Treatment of phosphaalkynes with coordinatively unsaturated transition metal species often results in oligomerization. Ususally the oligomer remains in the coordination sphere. However, the reaction of *t*-BuC≡P (**1**) with $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ affords the novel heterocycle, **2**.



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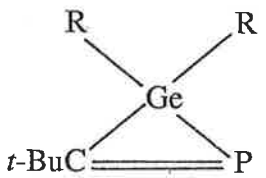

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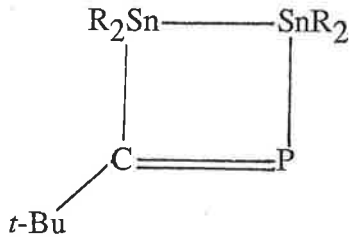

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Phosphaalkynes will also undergo cleavage reactions. Thus, reduction of $Ta(OAr)_2Cl_3$ (Ar=4-Me, 2, 6-*t*-$Bu_2C_6H_2$) with Na/Hg, followed by treatment with **1** results in formation of the 2,5-di-*t*-butyl-1,3,4-triphosphacyclopentadienyl and 2,4,5-tri-*t*-butyl-1,3-disphosphacyclopentadienyl anions. It is speculated that the formation of the former involves the phosphide intermediate, $(ArO)_2Ta{\equiv}P$.

The reaction of **1** with carbenoids also represents a rich source of new chemistry. For example, the reaction of **1** with germylene, $\{(Me_3Si)_2CH\}_2Ge$ affords **3**, the first example of a phosphagermirene. The stannylene, $\{(Me_3Si)_2CH\}_2Sn$ exists as a monomer/dimer equilibrium mixture in solution. Reaction of this mixture with **1** affords the phosphadistannacyclobutene, **4**. In principle **4** could be formed by either [2+2] cycloaddition of the dimer or via insertion of a second R_2Sn unit into an initially formed phosphastannirene. However, no spectroscopic evidence for the latter has been found.

S6

π-COORDINATION TO MAIN GROUP ELEMENTS - SOME NEW RESULTS.

P. Jutzi

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The π-coordination chemistry of s- and p-block elements is dominated by compounds with diverse cyclopentadienyl [1,2], carbollyl [1,3] and arene [1,4] ligands. Typical examples from the first two classes of compounds are presented.

I. π-Cyclopentadienyl complexes of the group 14 elements silicon, germanium, tin, and lead in their +2 oxidation state are stabilized by permethylation of the Cp ring. The synthesis, structure, and bonding of the metallocenes $(Me_5C_5)_2El$ [El=Si, Ge, Sn, Pb] is discussed. Furthermore, the synthesis, structure, and reactivity of the π-complexes $Me_5C_5GeCH(SiMe_3)_2$ and $Me_5C_5GeC(SiMe_3)_3$ is described.

II. Half-sandwich cyclopentadienyl complexes of the type $(Me_4C_5H)Me_2Si(Me_4C_5)El^+X^-$[El=Ge, Sn] show an additional weak metal-olefin interaction; their metallocenophane-like structures are proved by crystal structure analyses.

III. Carbollyl ligands have been successfully used as π-ligands in the chemistry of group 13, 14, and 15 elements. The synthesis and structure of $Me_2C_2B_9H_9Tl_2$, $Me_2C_2B_9H_9ElCl^-$ Ph_3PMe^+ [El=Ge, Sn] and $Me_2C_2B_9H_9ElR$ [El=P, As; R=Hal, Alkyl] is given.

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THE BIOLOGICAL ESSENTIALITY OF NICKEL

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S8

Mo and Mn *K* and *L* X-RAY ABSORPTION

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The 54-pole wiggler line at the SSRL allows high resolution spectroscopy down to 2 keV in a helium atmosphere. Molybdenum L_2 and L_3 edges have been recorded using this line and analyzed in terms of ligand field theory. Tetragonal complexes such as $[P(Ph)_4][MoOCl_4(H_2O)]$ exhibit four distinct $p \rightarrow d$ transitions in the second derivative spectra. X-ray splittings were related to optical transitions by a semi-empirical correlation scheme, using Racah parameters to correct for exchange and Coulomb interactions. The variation in band intensity with single crystal orientation helped confirm the assignments. Preliminary applications to molybdenum enzymes will be reported.

The U-4B SCM beam line at NSLS permits high resolution spectroscopy in the 200-1000 eV range, where 3d transition metal *L*-edges occur. Spectra for Mn model complexes, from simple $KMnO_4$ to tetranuclear clusters, have been obtained using electron yield detection. Using a special Ge detector with thin film diamond windows, we have also obtained preliminary soft x-ray fluorescence excitation spectra. Based on this experience, prospects for biological applications of this region will be discussed. The dramatic differences between *K* and *L*-edges, as well as between *L*-edges of 3*d* and 4*d* metals, are illustrated below. The status of theoretical calculations to account for *L*-edge spectra will be discussed.

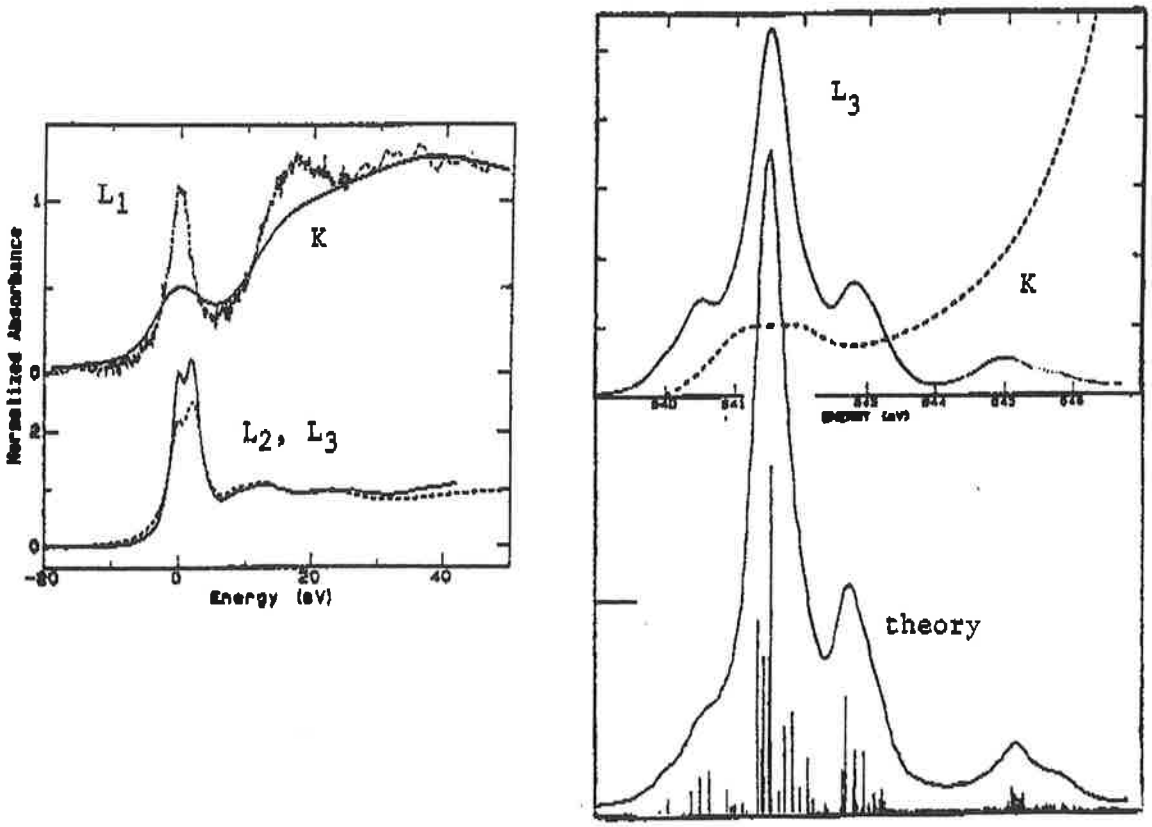

Figure - Comparison of *K* and *L* edge spectra for (left) Na_2MoO_4 and (right) $MnCl_2$.

SIMULATION TO THE NITROGEN CYCLE IN A MICROBIAL SYSTEM

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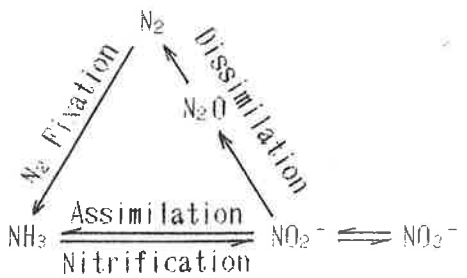
Inorganic nitrogen compounds, N_2, NH_3, NO_3^-, and so on, are circulating in the natural world according to the nitrogen cycle (Scheme). Molybdenum is considered as active sites not only in nitrogenases but also in nitrate reductases, the latter of which reduces NO_3^- to NO_2^-. The NO_2^- anion is further reduced to NH_3 and N_2 by assimilatory and dissimilatory nitrite reductases, respectively. These enzymatic reductions require multi-electrons. Such multi-electron reductions of those substrates can be performed by the use of an Fe-S or Mo-Fe-S cluster as catalysts under the controlled potential electrolysis conditions.

Scheme



Thus, the electrochemical reduction of $HOC_2H_4N_3$ with a $(n\text{-}Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$-modified glassy carbon electrode in H_2O at 1.25V vs. SCE affords NH_3 and N_2H_4 as eight- and six-electron reduction products (eqs. 1 and 2), respectively,

$$HOC_2H_4N_3 + 8H^+ + 8e^- \longrightarrow HOC_2H_4NH_2 + 2NH_3 \quad (1)$$
$$HOC_2H_4N_3 + 6H^+ + 6e^- \longrightarrow HOC_2H_4NH_2 + N_2H_4 \quad (2)$$

together with $HOC_2H_4NH_2$ and N_2 as two-electron reduction products. The turnover number for the formation of NH_3 based on the amount of the cluster attains more than 10000 in 2 h. The reduction of NO_3^- under the same electrolysis conditions yields NH_3 as an assimilation product (eq. 3) with the current efficiency of ca. 80% in H_2O at pH 10, where NO_2^- and NH_2OH were detected as reaction intermediates. On the other hand, the reduction of NO_2^- with the same electrode at -1.10V vs. SCE results in the formation of N_2O as an dissimilation product (eq. 4).

$$NO_3^- + 6H^+ + 5e^- \longrightarrow NH_3 + 3H_2O \quad (3)$$
$$2NO_3^- + 10H^+ + 8e^- \longrightarrow N_2O + 5H_2O \quad (4)$$

The function of other clusters, $[MoFe_3S_4(SR)_3(C_6Cl_4O_2)(solvent)]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$ (R=Ph and $C_6H_4\text{-}p\text{-}n\text{-}C_8H_{17}$), as catalysts for microbial nitrogen cycle model reactions will also be discussed.

S10

TWO, FOUR, FIVE-SHELL CLUSTERS AND COLLOIDS.

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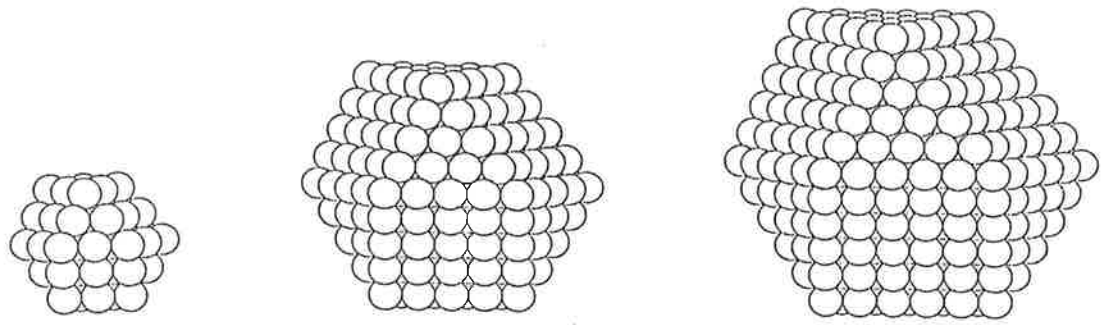
So called full-shell clusters consist of a magic number of metal atoms. Each shell in a cubic (ccp) or hexagonal (hcp) close packed structure contains $10n^2 + 2$ atoms (n = number of the shell). We have been able to prepare transition metal clusters with 55 (two-shell cluster), 309 (four) and 561 (five) atoms, each containing an appropriate ligand shell.



M_{55} M_{309} M_{561}

These large clusters can be imaged in a high resolution transmission electron microscope. For the first time also scanning tunnel microscopic pictures of five-shell clusters could be obtained. The chemical and physical properties are remarkably different from those of smaller clusters and of complexes. Conductivity measurements prove them as semi-conductors, magnetic measurements show the beginning of a bulk behavior. From ligand stabilized M_{55} clusters naked M_{13} clusters can be generated in solution which aggregate to superclusters $[(M_{13})_{13}]n$.

Colloids can be regarded as very large clusters with a certain distribution of the particle size (± 10%). We treated gold colloids with a diameter of about 17 - 18 nm with simple complex ligands like $Ph_2PC_6H_4$-SO_3Na in water solution and succeeded in a very good stabilization of the gold particles. They now can be isolated as a solid and are easily redissolved in water in any concentration to form blood-red solutions. By this method colloids can now be investigated in solid state or in concentrated solutions. TEM investigations prove them to be unchanged in size compared with the original particles.

FORMATION OF PLATINUM AND PALLADIUM CLUSTERS WITH CARBONYL PHOSPHINE LIGANDS

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The invitation for this Section Lecture was issued jointly to Professor Eremenko and to Professor Gubin.

S12

INTERSTITIAL NICKEL CARBONYL CLUSTERS

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Calculations on bare metal clusters of several metals systematically suggest that for an aggregate of thyrteen metal atoms the icosahedral geometry should be more favorable than the cuboctahedral or anticuboctahedral packing.|1| The opposite suggestion has been recently made on the basis of EHMO calculations on a $Rh_{13}H_{36}$ cluster.|2|

In the field of metal carbonyls there are known examples of tridecanuclear clusters possessing either an anticuboctahedral or icosahedral ($|Rh_{13}(CO)_{24}H_{5-n}|^{n-}$,|3| and $|Rh_{12}Sb(CO)_{27}|^{3-}$,|4|) assembly of metal atoms.These geometries apparently have the same electronic requirements, and the factors driving to the choice of one or the other are ill-defined.With the aim to experimentally gain some better understanding of this problem,we have undertaken systematic attempts to synthesize tridecanuclear clusters of general formula $|Ni_{12}E(CO)_x|^{y-}$,where E is either a different transition metal atom or a main group element.

As a result,we have isolated and characterized a series of Ni-Ir and Ni-Pt carbonyl clusters having the following formula: $|Ni_6Ir_3(CO)_{17}|^{3-}$, $|Ni_{12-x}Pt_x(CO)_{21}H_{4-n}|^{n-}$,$|Ni_{40-x}Pt_x(CO)_{44}H_{6-n}|^{n-}$ and $|Ni_{44-x}Pt_x(CO)_{48}H_{6-n}|^{n-}$.No tridecanuclear Ni-Ir and Ni-Pt carbonyl cluster has yet been obtained,and the metal frames of all the above species are related to fragments of close-packed metal lattices.In contrast,when using as heteroatom a main group element such as Ge,Sn and Sb a few centered icosahedral clusters have been isolated.A tentative interpretation of the above structural differences will be reported.

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4. J.L.Vidal and J.M.Troup,J.Organomet.Chem.,1981,213,351

CUPREDOXINS: CLASS OR CLASSES?

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Department of Inorganic Chemistry, University of Sydney, Sydney 2006

The lecture will use recent determinations of aminoacid sequences and structures to assess the similarities and differences between proteins which have "blue" or "type 1" copper centres. The proteins to be considered are the plastocyanins, azurins, 'pseudoazurin', cucumber basic protein, the "blue" copper subunit of ascorbate oxidase, stellacyanin, amicyanin, and the "blue" copper subunits of laccase, ceruloplasmin and cytochrome oxidase. The structures of the last five proteins are not yet known, and they are included in the comparison on the basis of reasonable inferences from the crystallographically determined structures of the first five proteins.

The term "cupredoxin" has been suggested by Adman [1] to denote that copper-proteins with "blue" copper centres generally appear to have a biological electron-transfer function. The use of a family name such as "cupredoxin" implies that the proteins are derived from a single ancestral protein, i.e., that they are products of 'divergent evolution'. This hypothesis has intuitive appeal and seems to have been accepted by many investigators. An alternative hypothesis is that "blue" copper centres in a variety of proteins have evolved from different starting points and represent independent optimum solutions to a variety of problems, i.e., that they are products of 'convergent evolution'. The relationships between the "blue" copper-proteins will be discussed in the light of these hypoptheses.

1. E.T. Adman *in* P.M. Harrison (ed.), *Topics in Molecular and Structural Biology. Metalloproteins*, Vol. 1, pp. 1-42 (Macmillan, London, 1985).

S14

COPPER CLUSTER ACTIVE SITES

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A coupled binuclear copper active site is found in a variety of proteins involved in oxygen binding (hemocyanin), activation (tyrosinase), and reduction to water (the multicopper oxidases). The unique absorption spectral features of oxy hemocyanin and tyrosinase are analyzed in detail and used to generate a spectroscopically effective model for the coupled binuclear copper active site (Fig. 1). These studies are then extended to the coupled (Type 3) site in the simplest multicopper oxidase, laccase. A Type 2 depleted form is characterized and used to generate a series of active site derivatives (deoxy [Cu(I)Cu(I)], half met [Cu(I)Cu(II)], met [Cu(II)Cu(II)]), which can be studied in parallel to analogous derivatives of hemocyanin. While there are general similarities, there are also important differences. In particular, the Type 3 site in laccase does not react with dioxygen in the absence of the Type 2 copper, and exogenous ligands do not bridge the two coppers of the Type 3 site. Low temperature MCD studies on the native enzyme are then presented which demonstrate that exogenous ligands in fact bridge between the Type 3 and the Type 2 copper centers defining a new trinuclear copper cluster active site (Fig. 2) which appears to be critical for O_2 reactivity of this enzyme.

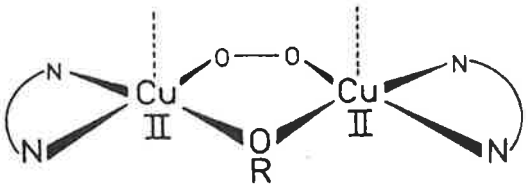

Figure 1. Oxy-Coupled Binuclear Copper Site

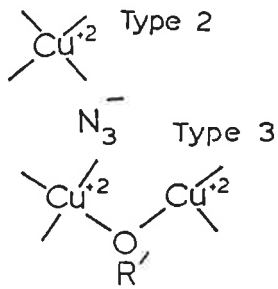

Figure 2. Trinuclear Copper Cluster Site

MECHANISTIC STUDIES ON THE BLUE COPPER PROTEIN PLASTOCYANIN

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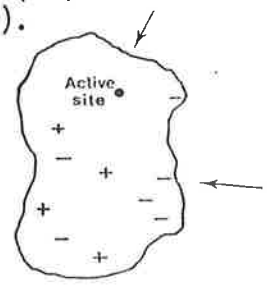
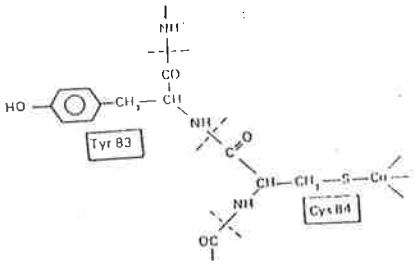
Plastocyanin (PC), structural information[1], is a single polypeptide protein of 99 amino acids (M_r 10,500) containing a single Cu active site with characteristic Type 1 properties, including intense blue colour ($\epsilon \sim 4500 M^{-1} cm^{-1}$ at 597nm) for the Cu(II) state. It is involved in chloroplast electron transport (370mV).



Studies with inorganic complexes have clearly established adjacent (~6Å) and remote (~15Å) binding sites in PC reactions[2]. Whereas the adjacent site is hydrophobic, the remote site has a high negative charge. The remote site is used by the physiological partner cytochrome f[3].

The attachment of $(NH_3)_5Ru$ to electron transport proteins has been carried out to explore fixed distance electron transfer from Ru(II) to Cu(II). For two His59 Ru-modified algal PC's (d 12A) the Ru(II) Cu(II) rate constant is $<0.3 s^{-1}$. This contrasts with studies on the unattached $Ru(NH_3)_5(imid)]^{2+}$, which is free to choose its own site for reaction, and gives $k>5x10^3 s^{-1}$[4]. The relative importance of negatively charged residues 42-45 and 59-61 as well as the protruding (highly conserved) Tyr83 at the remote site of PC has never been quite clear. The Ru study demonstrates that there is no favourable electron transfer route to the Cu.



Recent crystallographic information on ascorbate oxidase (AO)[5], having Type 1,2 and 3 Cu centres, has verified the remote site as relevant to biological electron transfer. Thus AO has a PC like domain with the O_2-binding Type 3 binuclear Cu's located at its remote site. Electrons have to be transferred from the Type 1 Cu to the O_2, and a through bond Cys His electron transfer path is defined. PC has an analogous CysTyr path as illustrated. Therefore Tyr83 is the focus for electron transfer reactions of PC.

Using $C(NO_2)_4$ spinach PC has been NO_2-modified at Tyr83. There is a shift in phenolic Tyr83 pK_a of two units to 8.1. The extra negative charge supplements the existing charge of the remote site in its reactivity. Using pulse radiolysis generation of the nitrophenyl radical, and intramolecular electron transfer to the Cu(II) site are being explored. Results for these and other related experiments will be reported.

It is suggested that Tyr can have a similar role to that of the heme in a cytochrome, and that appropriate interaction with the Tyr83 is required as a preliminary to electron transfer. S. obliquus PC has Phe for Tyr83 with no obvious loss in reactivity[6].

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S16

CARBON-HYDROGEN AND CARBON-CARBON BOND ACTIVATION WITH HIGHLY ELECTROPHILIC TRANSITION METAL COMPLEXES.

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Monomeric, coordinatively unsaturated (and hence, highly Lewis acidic) derivatives of scandium may be obtained with two pentamethylcyclopentadienyl groups as ancillary ligands. $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = H, alkyl) rapidly polymerize ethylene, and the kinetics of insertion of $CH_2{=}CH_2$ into Sc-R bonds have been examined. Treatment of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ with 2-butyne (1-3 M) proceeds by rate-determining β-H elimination to $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}H$ and olefin, followed by rapid insertion of 2-butyne to yield $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}C(CH_3){=}CH(CH_3)$. The relative rates of β-H elimination have been measured and a model for the transition state developed. With the less sterically encumbered scandocene hydrides, $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}Sc\text{-}H$ and $[\{(\eta^5\text{-}C_5H_3CMe_3)_2SiMe_2\}Sc\text{-}H]_2$, α-olefins are catalytically converted selectively ($\geq$95%) to the "head-to-tail" dimers, $CH_2{=}C(R)CH_2CH_2R$. Related catalytic cyclizations of α,ω dienes to the methylene cycloalkanes also proceed with very high selectivities. Methylene cyclobutane opens to 1,4-pentadiene at moderate temperatures, and under more forcing conditions isoprene is catalytically formed. The key steps in the ring opening and closure reactions, as well as for the introduction of skeletal rearrangements for 1,4-pentadienes are the insertion of olefin into the scandium-carbon bond and β-alkyl elimination. Quasi-living catalytic polymerizations of α olefins are effected by the related organoscandium derivatives with a cyclopentadienyl-amide ligand: $\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}Sc\text{-}R$.

MAKING AND BREAKING BONDS AT THE METAL CENTRES OF BIS (ORTHO CHELATED) ARYLMETAL COMPLEXES; MODEL REACTIONS AND CATALYSIS

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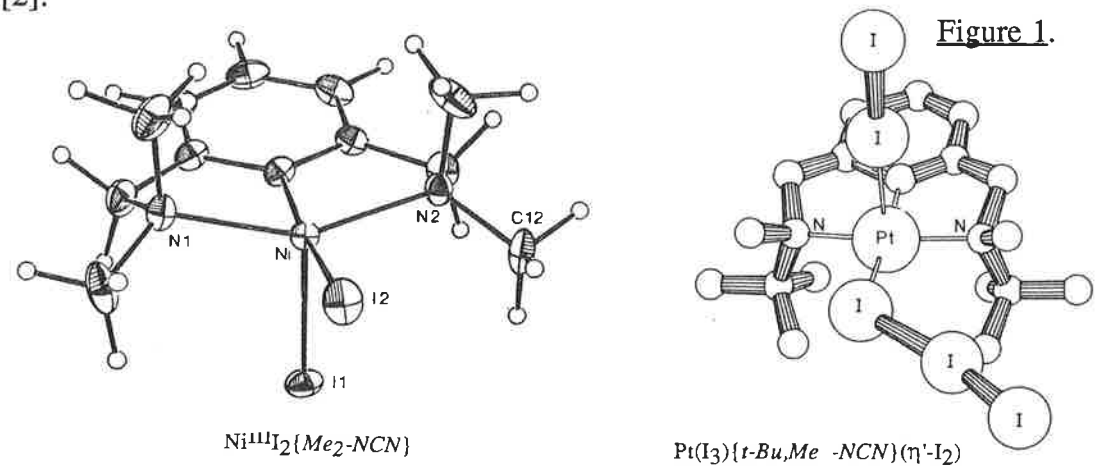
One of the most fundamental reactions in inorganic and organometallic chemistry is oxidative addition. It is a conceptually simple process in which a reagent, XY, reacts with a metal centre, M^{n+}, to form an $M^{(n+2)+}$ species with M-X and M-Y σ-bonds. Although this process and its reverse (reductive elimination) have been much studied in particular with metal-d^8 complexes, there is still considerable discussion regarding the question of whether, in a given system, oxidative addition occurs as a concerted two-electron transfer process involving a three centre M(XY) transition state or whether it involves two separate (non-concerted) one-electron transfers. In the latter case, the involvement of radical species is expected, and with metal-d^8 substrates this should result in the concomitant formation of paramagnetic metal species [1]. In our research, we follow an approach that involves the reaction of electrophiles X_2 (H_2, I_2) or XY (alkyl iodide, Me_2SnBr_2) with d^8-metal centres that are caught in a rigid and sterically well defined ligand system. These reactions have led to the isolation of stable compounds whose structural features mimick those found in the early stages of the reaction of electrophiles with the d^8-metal centre. Examples are shown in Figure 1[2].

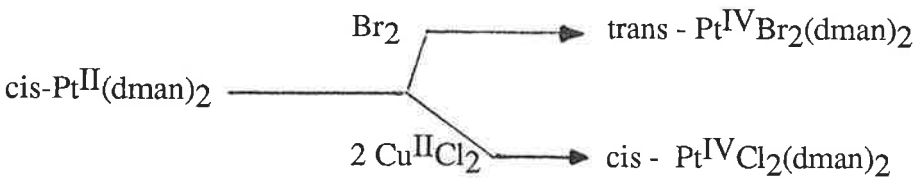
Figure 1.



$Ni^{III}I_2\{Me_2\text{-}NCN\}$ $Pt(I_3)\{t\text{-}Bu,Me\ \text{-}NCN\}(\eta'\text{-}I_2)$

Recently, we found that reactions of halogens, Cu(II) halides, and alkyl halides with d^8-metal centres (Pd, Pt, Ir) bonded to the 8-(dimethylamino)-1-naphthyl anion (abrreviated as dman) proceed along well defined routes to d^8-metal products, the stereochemistry of which reflect the type of mechanism involved [3]. One example, involving the reactions of cis-$Pt(dman)_2$ with Br_2 and $Cu^{II}Cl_2$ respectively, is shown in figure 2.

Figure 2.



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[3] J.A.M. van Beek, G. van Koten, to be published.

MODELLING CATALYTIC INTERMEDIATES WITH ORGANOPLATINUM COMPLEXES

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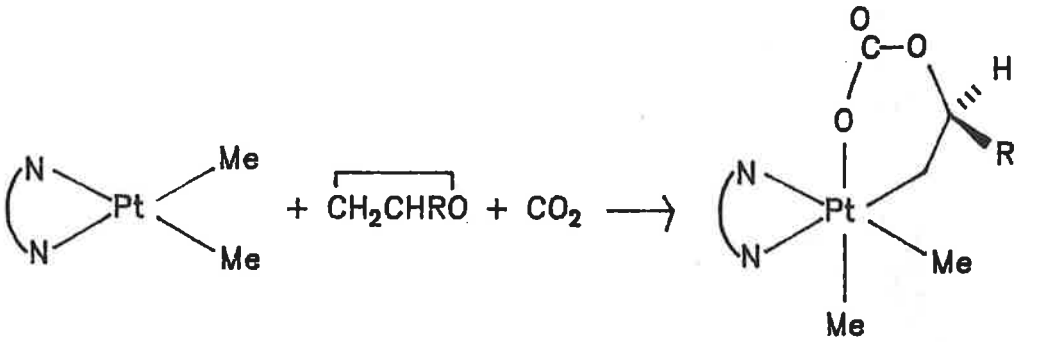
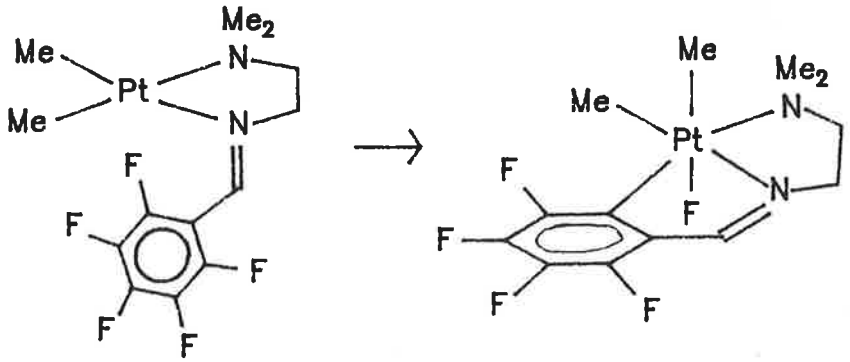
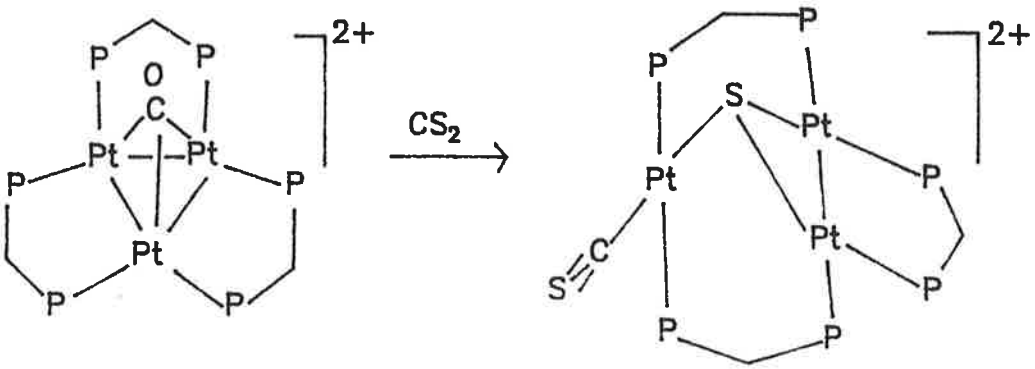
Recent results on the coordination and activation of small molecules by mononuclear or trinuclear organoplatinum complexes will be described. Normally unreactive bonds such as C-O, C-F or C=S can be activated by using enhanced reactivity due to ring strain, the chelate effect or the cooperative effects of two or more metal atoms, as shown in the equations.







Studies of reactivity and mechanism, based on kinetic studies, isotopic labelling and the spectroscopic detection of reaction intermediates will be described.

CHEMICAL AND BIOLOGICAL STUDIES OF POLYIRON-OXO COMPOUNDS

Stephen J. Lippard

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Polyiron-oxo centers occur in a number of interesting proteins, including the oxygen transport protein hemerythrin, isolated from marine invertebrates, ribonucleotide reductase, a bacterial and mammalian protein involved in the first committed step in the biosynthesis of DNA, methane monooxygenase, a hydroxylation protein isolated from soil bacteria, and purple acid phosphatase, an enzyme found principally in the uterine fluid of pregnant sows. A common chemical feature in all of these proteins is a bimetallic center in which two iron atoms are linked by one or more bridging ligands including an oxo or hydroxo group. We have chemically synthesized models for the active sites of these proteins that mimic well their structural, spectroscopic, and magnetic properties. More recently, we have been using binucleating ligands to prepare more closely biomimetic systems. In addition we have obtained molecules that are capable of binding substrate and have studied the catalytic oxidation of hydrocarbons by molecular oxygen at room temperature and pressure using chemistry involving binuclear iron complexes and appropriate reducing agents. Direct studies of component A proteins of methane monooxygenase from two sources have also been carried out, revealing features of the molecular geometry and electronic structure of their diiron cores in the three accessible, Fe(III)Fe(III), Fe(III)Fe(II), and Fe(II)Fe(II), oxidation states.

Ferritin is the protein responsible for iron storage in most life forms. The core of ferritin is comprised of a hollow sphere into which can be packaged up to 4500 iron atoms in a polyiron-oxo-hydroxo array. Detailed information about the chemical and structural composition of the iron aggregates that comprise the ferritin core is lacking. We have approached this interesting problem through model chemistry, investigating the assembly of polyiron-oxo-hydroxo species through controlled, stepwise synthesis of crystalline aggregates, the structures of which are determined by X-ray crystallography. Aggregates containing 3, 4, 6, 11, and 17 oxo- and hydroxo-bridged metal atoms have been synthesized and characterized. The chemistry and topology of interconversions among these species have been investigated and will be discussed with reference to ferritin core formation.

This work has been carried out with the excellent assistance of co-workers W.H. Armstrong, R.H. Beer, J.G. Bentsen, S.G.Bott, X. Feng, S.M. Gorun, W. Micklitz, R.L. Rardin, M.E. Roth, A.R. Spool, W.B. Tolman, and P. Turowski. We thank the National Institute of General Medical Sciences for financial support.

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METAL AND ANION BINDING SITES IN LACTOFERRIN AND RELATED PROTEINS

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The control of iron levels in biological systems depends on the presence of a variety of specific chelators. In vertebrates this role is filled by a family of proteins, the transferrins, which have the ability to bind, tightly and specifically ($K \sim 10^{20}$) two Fe^{3+} ions per molecule. A feature of the binding is the absolute requirement for the simultaneous binding of two CO_3^{2-} (or HCO_3^-) ions.

The structural basis for this synergistic anion-cation relationship and for the great stability of the iron-protein complex has been addressed through crystallographic studies on human lactoferrin (Lf) [1,2]. The three-dimensional structure of Fe_2Lf has been determined and refined at 2.2 Å resolution. The molecule is organised into two globular lobes, the N-lobe (residues 1-332) and the C-lobe (residues 344-691), each carrying a single iron site. The two iron sites are essentially identical, each Fe^{3+} ion bound to four protein groups (2 Tyr, 1 Asp, 1 His) and the CO_3^{2-} anion. The anion acts as a spacer between the cation and positively charged groups on the protein, with which it is involved in a precise array of hydrogen bonds.

These observations may now be used to re-examine spectroscopic and chemical results. The construction of the iron site suggests a mechanism for iron binding and release which also has implications for the binding of cations other than Fe^{3+} and anions other than CO_3^{2-}. Some preliminary results on copper-lactoferrin will be presented.

The results from the lactoferrin structure analysis can be extended to other iron-binding proteins. Finally, the anion site in lactoferrin shows a remarkable similarity to the SO_4^{2-} site in a bacterial sulphate-binding protein; this relationship, which suggests common design features in ion-binding proteins, will be explored further.

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Magnetic Circular Dichroism of Iron-containing Metalloproteins

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From various bacterial sources a range of low-molecular weight, water soluble ferredoxins (Fd) have been isolated which contain seven iron atoms and eight suphide ions arranged as two redox active iron-sulphur clusters of stoichiometry $[Fe_3S_4(cys)_3]^{2-,3-}$ and $[Fe_4S_4(cys)_4]^{2-,3-}$. The three iron cluster has recently been confirmed by X-ray crystallography to have the same structure as the cubane four-iron cluster less one iron atom and its associated cysteine ligand. The magnetic, optical and electrochemical properties of the [3Fe-4S] core cluster in two seven-iron ferredoxins, Fd I *Azotobacter chroococcum* (*A.c.*), and Fe III, *Desulphovibrio africanus* (*D.a.*), wil be described. The former Fd contains nine cysteines in its sequence while the latter contains only seven.

The [3Fe-4S] core cluster in Fd I, *A.c.* undergoes a one-electron reduction process at -460 ± 10 mV vs NHE which is linked to cluster protonation with a pK_a = 7.8. Spectroscopic evidence is used to discuss the site of protonation. This process is unique to *Azotobacter* Fd I amongst three-iron clusters. A redox-linked protonation process may have physiological significance.

When reduced the $[3Fe\text{-}4S]^0$ core cluster in Fd III *D.a.* rapidly takes up ferrous ion and an electron to form a $[4Fe\text{-}4S]^{1+}$ core cluster. Since only three cysteine residues are available the fourth ligand must be either water or an amino-acid side-chain other than cysteine. Sequence data suggests it to be the carboxylate group of aspartic acid. This cluster has, in the reduced state, atypical magnetic properties, the electronic spin being S=3/2. This is the first well authenticated example of a [4Fe-4S] cluster with non-thiolate ligation in protein.

NOVEL ASPECTS OF ELECTROCHEMICAL OXIDATION OF INORGANIC COMPOUNDS IN NON-COORDINATING MEDIA

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Redox processes are an important class of chemical reaction. In the case of chemical oxidation, the chemical oxidant often plays a specific role in the overall process. For example, oxidative addition reactions such as

$$[Pt(II)Cl_4]^{2-} + Cl_2 \longrightarrow [Pt(IV)Cl_6]^{2-} \qquad (1)$$

in which the co-ordination number of the metal increases after oxidation are very common. The reverse of the example given in equation 1 in which ligand loss accompanies a decrease in oxidation state is called reductive elimination. Electrochemical oxidation reactions may differ from chemical oxidation, in that ligands may not be available, so that highly reactive co-ordinatively unsaturated compounds designated as $[B]^{n+}$ in equation 2 are likely to be generated after an electron transfer process involving oxidation of compound A.

$$A \rightleftharpoons [B]^{n+} + ne^- \qquad (2)$$

In contrast electrochemical reduction processes such as

$$[PtCl_6]^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^- \qquad (3)$$

are very likely to follow their analogous chemical reduction pathways since elimination of a ligand can take place in both cases.

In this paper, examples of a range of electrochemical oxidation processes of inorganic compounds will be given to emphasise the novel aspects arising from the use of this method of oxidation. In particular, experimental techniques for obtaining data in non-coordinating media will be reviewed as will the role of the electrolyte when highly reactive and co-ordinating unsaturated compounds are generated at an electrode surface. Examples used to illustrate the principles of electrochemical oxidation in non-coordinating media such as chlorinated and aromatic hydrocarbons include the oxidation of metals to their metal cations (non-solvated (?)) and oxidation of zero valent six-coordinate metal carbonyl complexes.

Acknowledgements The work described in this paper has involved extensive collaboration with colleagues from numerous laboratories. Their contribution and financial assistance from the Australian Research Council are gratefully acknowledged.

THE ELECTROCHEMISTRY OF METALLOPROTEINS

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There is now no difficulty in obtaining the *direct* electrochemistry of metalloproteins, whether at modified electrodes, with additional metal ions in solution, or even at normal electrode surfaces. All that is required is some method of ensuring that the protein is held long enough at the electrode surface for electron transfer to occur. Recently, we have been examining the electrochemistry at microelectrodes, whether deliberately designed electrodes or ones adventitious in size.

The electrochemistry of protein-protein complexes has posed problems, not only for the details of its structure on the electrode surface but also for the nature of the complex itself. From related studies on the nuclear magnetic resonance spectroscopy of the complexes, it appears that a mobile, dynamic structure is more compatible with the structure of the complex in solution.

With enzymes, there appeared to be some difficulty. Indeed, it was in the midst of unsuccessful attempts to achieve direct electrochemistry that *indirect* electron transfer to various enzymes was achieved using ferrocenes as mediators. The major advantages of the latter were that, not only did they react fast with most redox enzymes but they competed successfully with dioxygen, often the natural substrate. In addition, there were many ferrocenes! Consequently, the mediator could be selected on account of, e.g., its redox potential, solubility or its ease of immobilisation. Many of these factors were important when it was decided to manufacture a glucose sensor for home use by diabetics.

It has finally been possible to achieve the *direct* electrochemistry of metalloenzymes, i.e., without mediation. Care must be taken ensuring that the electrode and the enzyme are compatible but the electrochemistries of e.g. *p*-cresolmethylhydroxylase, lactate dehydrogenase and hydrosulphide oxidoreductase are well behaved.

SPECTROELECTROCHEMISTRY AND CHEMISTRY OF METALLOPORPHYRINS.

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The combined application of thin-layer UV-visible, FTIR, and ESR spectroelectrochemical techniques to monitor the redox reactions and associated chemistry of various transition metal porphyrins is presented. A given metalloporphyrin complex may be oxidized or reduced at the central metal ion, at the porphyrin π ring system, or at one of the axially coordinated ligands. The site of electron transfer and the overall number of electrons transferred in a given step depends upon the nature of the specific porphyrin complex as well as upon properties of the solvent/supporting electrolyte system. Some metalloporphyrin electrode reactions are chemically and electrochemically reversible but others are coupled with one or more homogeneous chemical reactions. The use of thin-layer spectroelectrochemistry allows one to obtain information as to the site of electron addition or abstraction, the oxidation state of the electrogenerated species, and the nature of any coupled chemical reactions on time scales of 10-30 seconds. Examples of thin-layer ESR, FTIR, and UV-visible spectra which were obtained for several different metalloporphyrin systems are presented and the data from these techniques is compared to data obtained by classical methodologies. Construction of the thin-layer cells is also presented and the thin-layer behavior of each cell is demonstrated for both ferrocene oxidation and metalloporphyrin oxidation-reduction in nonaqueous media. Each thin-layer cell can be utilized to rapidly perform in situ coulometry and cyclic voltammetry. In addition, the thin-layer ESR cell can be utilized to obtain spectra at both low and room temperature.

POLYTOPIC CHIRAL BINDERS

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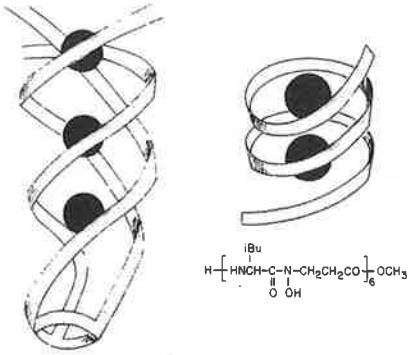
Two families of helical complexes that accommodate several metal ions in a string of octahedral ion binding cavities are described: triple-stranded helices and single stranded helices.



These extensions are achieved by the sequential addition of identical monomers that contain terminal amino and carboxyl groups, a natural amino acid of defined absolute configuration and a hydroxamate group.

$$H_2N\text{-}CHR\text{-}(CH_2)_n\text{-}CONOH\text{-}CH_2CH_2\text{-}COOH \qquad n = 0, 1, 2$$

The terminal functional groups allow for ready coupling through amide bond formation, the amino acid residues provide lipophilicity and chirality, and the hydroxamates serve as binding sites.

The formation of helical arrangements in preference to random structures is attributed to hydrophobic interactions and networks of inter-strand H-bonds between amide linkages.

Criteria for identifying helical structures will be given and their potential for the generation of chiral receptor sites and artificial channels indicated.

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MACROCYCLE-MEDIATED SEPARATIONS USING LIGAND-BONDED SILICA GEL AND DUAL MODULE HOLLOW FIBER MEMBRANES

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Macrocycles are noted for the remarkable selectivities which certain of them show toward metal ions. This selectivity has been studied extensively for free macrocycles in single solvent systems. However, there is a need for new systems that are more economical and with engineering feasibility which incorporate macrocycles to perform actual separations. Recently, we have taken a major step in meeting this need by attaching macrocycles to silica gel by a covalent linkage. This silica gel-bound macrocycle (SGBM) material is effective in making cation separations while maintaining the SGBM for re-use. Prediction of selectivities with this SGBM material requires a knowledge of log K values for the SGBM-metal ion interaction. These log K values have been measured for a variety of SGBM-metal ion systems. The values are found to be similar to those for metal ion interaction with free macrocycles. The use of the log K values to predict separations is illustrated with several systems including bound crown ethers and bound aza macrocycles.

A new type of dual module hollow fiber system has also been developed which allows excellent separations to be accomplished without the disadvantages of traditional macrocycle-mediated liquid membrane separation systems. Advantages of the improved system include the use of solvents and macrocycles of low hydrophobicity. Examples of the separations of cations using crown ether and triazolo macrocycles will be described. Separations involving alkali cations, alkaline earth cations, transition metals, and Pb^{2+} will be included.

POLY-AZA MACROCYCLIC COMPLEXES THAT TRANSPORT ELECTRONS ACROSS LIQUID MEMBRANES

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Transition metal complexes can be used as carriers for the transport of electrons from an aqueous phase containing an oxidizing agent (Electron Source Phase, ESP) to an aqueous phase containing an oxidizing agent (Electron Receiving Phase, ERP), across a layer of a water immiscible solvent (the *bulk liquid membrane,* e.g. dichloromethane).

A convenient redox system to be used as an *electron carrier* is represented by the Ni^{II},Ni^{III} complex of *N*-cetylcyclam (L), a lipophilic version of the well known 14-membered macrocycle [1]. In particular, since the potential associated to the $NiLX_3/NiLX_2$ redox couple in dichloromethane is strongly dependent upon the nature of the X^- anion, electron transport experiments can be switched on/off by changing the type of the background electrolyte NaX present in ESP and ERP. In particular, aqueous peroxydisulfate oxidizes Ni^{II} to Ni^{III} at the ERP/membrane interface in the presence of chloride ions, but does not work in the presence of the less coordinating perchlorate ions. The oxidized carrier $NiLX_3$ is reduced at the other side of the membrane by aqueous metal centered reducing agents (e.g. Fe^{II}, Ti^{III}, Cr^{II}), but is not reduced by non-metal reducing agents (e.g. I^-). Moreover, the rate of the two-phase reduction process, and that of the overall electron transport experiment, vary in a spectacular way according to the type of the reducing agent. This allows to perform selective oxidation of reducing agents present in a mixture: in particular, using the described three-phase device, it is possible to oxidize, using persulfate, the Ti^{III} ion, leaving intact the stronger reducing agent Cr^{II} ion, present in the same solution.

The design of further redox systems, in which a transition metal ion is coordinated by lipophilic multidentate ligands of varying nature and coordinating tendencies, to be used as carriers for the *selective* transport of electrons across liquid membranes, will be presented and discussed.

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INTERMOLECULAR FLUORINE ATOM ABSTRACTION BY DIVALENT LANTHANOID COMPLEXES AND UNUSUAL DIVALENT LANTHANOID-METHYL CLUSTER COMPLEXES.

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Divalent lanthanoid complexes abstract fluorine atoms from unsaturated perfluorocarbons giving isolable trivalent lanthanoid fluoride complexes and multiply unsaturated fluorocarbon products, plus products which result from coupling and hydrogen atom abstraction. The rates of many of these reactions are remarkably fast. Abstraction of fluorine from less reactive substrates such as perfluoro-benzene are shown to be accelerated by visible light. The mechanisms of these reactions will be discussed including qualitative comparison of the rates of fluorine abstraction by bis(pentamethylcyclopentadienyl)-europium, -samarium and -ytterbium complexes. Three trivalent ytterbium-fluoride product complexes are characterized by X-ray crystallography including a penta-ytterbium fluoride cluster.

The synthesis of divalent tri-ytterbium and hexa-ytterbium methyl complexes is reported, together with characterization by multinuclear NMR, including ^{171}Yb NMR. The first examples of ^{7}Li-^{171}Yb and ^{13}C-^{171}Yb NMR are observed in these complexes. The structures of these complexes are compared with other lanthanoid oligomers with bridging alkyl groups.

METAL CATALYSED HOMOGENEOUS OXIDATION PROCESSES

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Oxidation is one of the most common industrial chemical processes. In the laboratory many different oxidants are used, but in large scale reactions for economic reasons air is the most common reagent. Exceptions occur when specific functional groups are required, as in chlorination reactions. The reactions of dioxygen are often slow, however, so that they are usually catalysed, often by metal compounds.

Some aspects of metal catalysed homogeneous oxidation processes are illustrated by our work on the destructive oxidation of organochlorine wastes catalysed by ruthenium compounds. Many organochlorine molecules such as DDT and the PCB's are persistent environmental poisons. Although their manufacture has virtually ceased, there are substantial stocks both in use and in storage which require proper disposal. At present high-temperature incineration is the only accepted method for the disposal of these materials. Homogeneous oxidation is chemically equivalent to incineration if the consumed oxidant is oxygen. The products of complete oxidation are carbon dioxide and hydrochloric acid, or carbonate and chloride.

Catalytic oxidation by ruthenium tetraoxide has been shown to be an effective reaction for the destructive oxidation of chlorinated aromatics. For the reaction in alkaline solution hypochlorite is used as a convenient oxidant. Even though bleach is relatively inexpensive, the economics of the process are in part determined by the stoichiometry. For the complete oxidation of a mole of hexachlorobenzene:

$$C_6Cl_6 + 9\ Cl_2 + 30\ NaOH \longrightarrow 6\ NaHCO_3 + 24\ NaCl + 12\ H_2O$$

One tonne of C_6Cl_6 requires about 2 tonnes of Cl_2 and 4 tonnes of NaOH.

To reduce costs oxidation by oxygen is desirable. This eliminates the cost of the chlorine and also generates some of the base required:

$$O_2 + 2H_2O + 4\ e^- \longrightarrow 4\ OH^-$$

Oxygen in alkaline solution, however, does not efficiently regenerate the active RuO_4 catalytic species. One solution is to conduct the two reactions separately in an electrocatalytic process. Efficient electrodes for the reduction of oxygen to water are available. With a small applied voltage the ruthenium catalyst can be reoxidised at the anode and the electrocatalytic oxidation of organochlorines accomplished.

VERSATILE CATALYSIS OF $RhCl(CO)(PMe_3)_2$ VIA C-H BOND ACTIVATION

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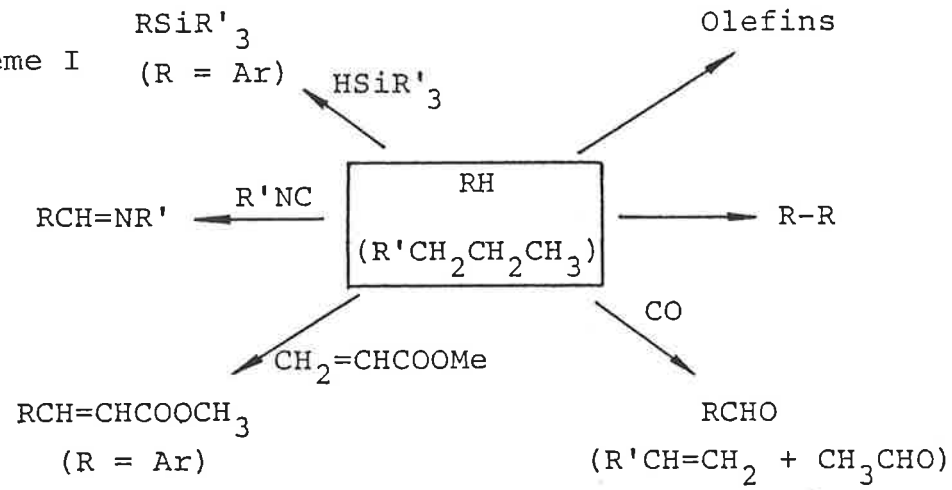
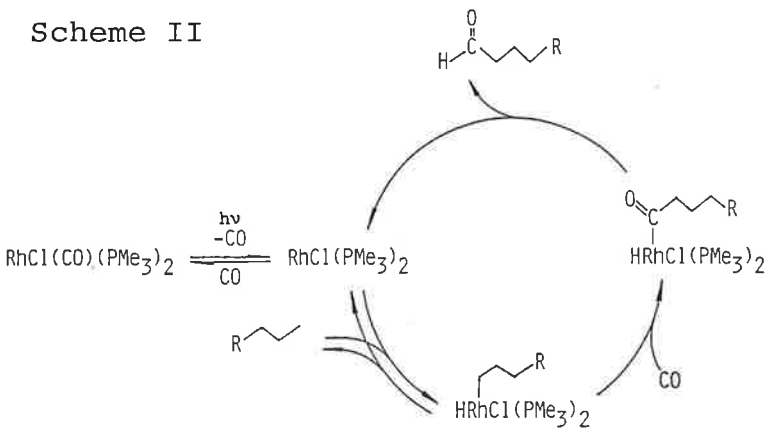
Direct functionalization of arenes and alkanes has been achieved via C-H bond activation in the presence of transition metal complexes under irradiation (λ > 300 nm). Rhodium complexes, in particular $RhCl(CO)(PMe_3)_2$, are powerful catalysts for the synthetic reactions illustrated in Scheme I [1].

Scheme I



Some of these reactions are highly catalytic (turnover frequencies up to 200 h^{-1}). A reaction mechanism involving photo-assisted dissociation of the CO ligand is envisaged (Scheme II). Besides this, however, the irradiation is presumably playing an important role to drive the catalytic cycle. Mechanistic consideration with particular emphasis placed on the alkane dehydrogenation will be given.

Scheme II



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PLATINUM COORDINATION CHEMISTRY WITH NUCLEOBASES

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Among Pt complexes of nucleobases, those containing the pyrimidine bases uracil and thymine display a particularly rich coordination and redox chemistry. The lecture will focus on two topics of this chemistry.

(i) Oxidation products of di- and trinuclear complexes of types cis-$[a_2PtL_2Pta_2]^{2+}$, cis-$[a_2PtL_2PtaCl]^{+}$, cis-a_2PtL_2-$PtCl_2$ and cis-$[a_2PtL_2PdL_2Pta_2]^{2+}$ with L = 1-methyluracil and/or 1-methylthymine anion and a = NH_3 and/or cyclopropylamine or a_2 = en, bpy, o-phen. Compounds isolated and structurally characterized include tetranuclear spezies with Pt(2.25) and Pt(2.5) average oxidation states, mixed [Pt(II) Pd(III)Pt(II)] complexes, diplatinum(III) and mixed $[Pt(III)]_2$,Pt(IV) complexes. This chemistry is neither paralleled by the corresponding Pd(II) analogues, related Au(III) complexes nor by trans-Pt(II) compounds. The uniqueness of the cis-a_2Pt(II) entity results from a combination of favorable geometry (relative positions of exocyclic oxygens of L ligands), high basicity of these sites, and ready oxidizability of the metal.

(ii) Mixed nucleobase complexes. Complexes of composition cis-$[a_2PtL_1L_2]^{n+}$ (L_1 = uracil or thymine, L_2 = other nucleobase) may be considered models for cross-links of two oligonucleotide strands. Formation, structure and reactivity of these compounds will be discussed.

PREPARATION AND STRUCTURE OF A CYANONITRIDOTECHNETIUM(V) COMPLEX, $[AsPh_4]_2[TcN(CN)_4(H_2O)]\cdot 5H_2O$

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The nitrido ligand (N^{3-}) is a powerful π-electron donor which tends to stabilise transition metals in high oxidation states. A variety of nitridotechnetium complexes based on the $Tc^{VI}N^{3+}$, $Tc^{V}N^{2+}$ or $[NTc^{VI}\text{-}O\text{-}Tc^{VI}N]^{4+}$ cores have been prepared and structurally characterised by X-ray diffraction.

The reaction of $[AsPh_4][Tc^{VI}NCl_4]$ with KCN and added $AsPh_4Cl$ in CH_3CN/H_2O gave yellow water soluble crystals of $[AsPh_4]_2[Tc^{V}N(CN)_4(H_2O)]\cdot 5H_2O$ in good yield. The complex crystallises in the monoclinic space group $P2_1/n$ with a = 17.107(5), b = 19.965(7), c = 15.473(5) Å, β = 101.70(2)°, with Z = 4. The structure consists of $[AsPh_4]^+$ cations and $[TcN(CN)_4(H_2O)]^{2-}$ anions. The geometry is distorted octahedral with a water molecule coordinated trans to the nitrido ligand (Tc-O distance, 2.559(10) Å). The TcN bond distance is 1.593(11) Å. The cyano ligands occupy the four equatorial positions and their geometry is as expected. The $[AsPh_4]_2[TcN(CN)_4(H_2O)]\cdot 5H_2O$ structure differs markedly to that of $K_2[ReN(NC)_4]\cdot H_2O$ where the Re and nitrido atoms are arranged in infinite chains [1].

The reaction of $Cs_2[Tc^{VI}NCl_5]$ (d^1) with aqueous KCN results in a yellow solution which does not show e.s.r. signals. Addition of conc. HCl to this solution results in the formation of a number of e.s.r. active species which on standing convert to $[TcNCl_4]^-$. Whether the yellow solution contains Tc^{V} or diamagnetic Tc^{VI} species is not clear, but the formation of $[AsPh_4]_2[TcN(CN)_4(H_2O)]\cdot 5H_2O$ shows that reduction of Tc^{VI} to Tc^{V} may occur in the presence of CN^-. A solution of $[AsPh_4]_2[TcN(CN)_4(H_2O)]\cdot 5H_2O$ in HCl, on heating, gives $[AsPh_4][TcNCl_4]$ in low yield. These results show that interconversion of TcN^{3+} and TcN^{2+} cores occurs under appropriate conditions.

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Nonionic Macrocyclic Gadolinium(III) Complexes As Contrast Agents in Magnetic Resonance Imaging

M. Tweedle, H. Brittain, C. Chang, D. Dischino, J. Emswiler, G. Gaughan, J. Telser, P. Wedeking

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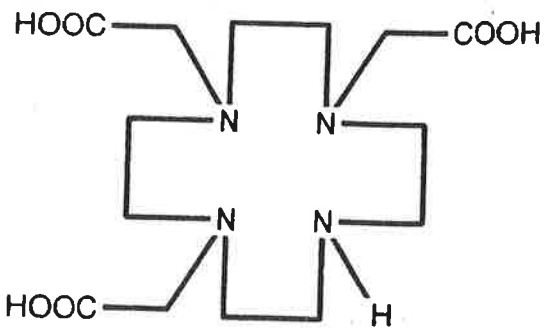
Intravenously administered Gd(III) complexes catalyze the relaxation of bulk water protons in living tissues and are indirectly detectable in magnetic resonance images at submillimolar concentration. Ideally, Gd(III) complexes for this purpose should be highly water soluble ($\geq$ 0.5 M), thermodynamically stable and kinetically inert *in vivo*, rapidly excreted, and well tolerated. A series of new Gd(III) complexes has been synthesized and characterized. The new parent ligand, DO3A (1,4,7 - triscarboxymethyl - 1,4,7,10 - tetraazcyclododecane) was prepared through a simple new route via a mono-protected 1,4,7,10-tetraazadodecane. A variety of R-DO3A derivatives were prepared by substitution of the unique nitrogen of DO3A (1). These and other Gd(III) complexes will be discussed in terms of the chemical attributes which lead to the desired physical and biological properties.



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S34

ASYMMETRIC CATALYSIS, PRINCIPLES AND PERSPECTIVES

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Transition metal mediated asymmetric catalysts provide one of the more elegant solutions to the production of pure chiral molecules. The idea that small quantities of self-regenerating chiral material can produce large quantities of chiral material is intellectually appealing although it does not necessarily follow that such processes are economically viable. It is perhaps surprising that certain optically pure amino acids, for example, are more economically produced by spontaneous resolution than by asymmetric catalysis. Even so, it is remarkable how quickly the method of asymmetric catalysis has been transferred from academic laboratories to industrial production. The impetus for this transfer is probably related to the recent shift from decreasingly profitable commodity chemicals to "high value added" speciality products. The scientific "push" and the industrial "pull" seem to have coincided for asymmetric catalysis and was reinforced by the regulatory demands for enantiomerically pure products.

The lecture describes examples of asymmetric catalysis which are now or are about to be applied commercially. It turns out that, in the main, these examples happen to be those which are currently of greatest scientific interest. The discussion of these examples will primarily center on the mechanisms of catalysis. The following examples will be reviewed:

- ◊ Cyclopropanation - insecticides, antibacterials
- ◊ Epoxidation - phermones, ß-blockers
- ◊ Double bond migration - flavors, fragrances
- ◊ Hydrogenation - amino acids, vitamin E
- ◊ Polymerization - isotactic polymers
- ◊ Allylation - vitamin E

NEW CHIRAL RUTHENIUM COMPLEXES FOR ASYMMETRIC CATALYTIC HYDROGENATIONS

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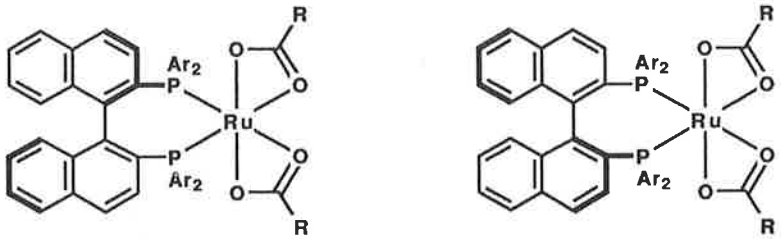
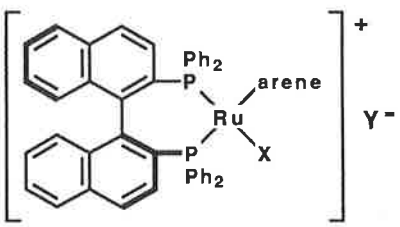
Homogeneous asymmetric hydrogenation of olefins catalyzed by chiral transition metal complexes provides a powerful means for preparing optically active organic compounds. We have developed chiral diphosphine ligand BINAP (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) and showed that BINAP—Rh(I) complexes are highly efficient catalysts for asymmetric hydrogenation of α-acylaminoacrylic acids and asymmetric conversion of prochiral allylamines into enamines. Recently, we have prepared mononuclear BINAP—Ru(II) complexes **1** [1]. The crystal structure of Λ-(S)-**1** (R = $(CH_3)_3C$, Ar = C_6H_5) has been determined by X-ray analysis, which revealed interesting strutural characteristics of **1**. These complexes serve as highly efficient catalysts for asymmetric hydrogenation of various enamides, α,β- and β,γ-unsaturated carboxylic acids, allylic and homoallylic alcohols, and α-amino ketones, etc.



Ar = C_6H_5, *p*-$CH_3C_6H_4$
R = CH_3, $(CH_3)_3C$, CF_3

We have also prepared new cationic BINAP—Ru(II) complexes **2** in high yields by the treatment of arene—RuX_2 complexes with (S)-BINAP or by anion exchange reaction of the resulting complexes with $AgBF_4$ or $NaB(C_6H_5)_4$ [2]. The molecular structure of **2** (X = Cl, Y = BF_4, arene = C_6H_6) has been determined by X-ray analysis. These complexes are highly efficient catalyst precursors for asymmetric hydrogenation of β-functionalized ketones, allylic alcohols, α,β-unsaturated carboxylic acids, etc.



(*S*)-2

X, Y = Cl, Br, I, BF_4, $B(C_6H_5)_4$
arene = C_6H_6, *p*-$CH_3C_6H_4CH(CH_3)_2$

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S36

HIGHLY STEREOSELECTIVE SYNTHESES OF ARSENIC AND PHOSPHORUS LIGANDS AND THEIR RELEVANCE TO ASYMMETRIC SYNTHESIS

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Asymmetric synthesis, once considered a rather exotic speciality in chemistry, is now a primary focus of activity for academic and industrial chemists. The asymmetric synthesis of one enantiomer or of a particular diastereomer of a substance is a very attractive proposition, because unlike a process involving a chemical resolution the yield can be 100%. Although dominated by organic chemists employing natural products as chiral auxiliaries, the field of asymmetric synthesis is wide open to coordination chemists, who, with their superior knowledge of ligands and the chelate effect, have before them unparalleled opportunities. The aim of this lecture will be to show that highly stereoselective syntheses of optically active and diastereomerically homogeneous tertiary arsines ($\underline{E}_{inv}$ > 40 kcal mol^{-1}) and tertiary phosphines ($\underline{E}_{inv}$ 30-35 kcal mol^{-1}) are now possible, and that it is realistic to design and manufacture sophisticated ligands based on these elements for use in asymmetric synthesis. As well as presenting some highlights of our work on the stereoselective synthesis of macrocyclic bis(tertiary arsines), recent developments concerning the synthesis of poly(tertiary phosphine) macrocycles and cages will be described. The use of a chelating bis(tertiary phosphine) platinum(II) auxiliary for the chemical differentiation of the enantiotopic terminal hydroxyl groups of glycerol will also be described, as will be the use of such auxiliaries for the complexation of 1,2-diols. In conclusion, it will be revealed that it may be feasible to produce practical quantities of optically active tertiary arsines by biological methods.

Supertripodal Ligands - Synthesis, Coordination Chemistry, and Possible Applications

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Effective design of chelating ligands requires organization of the binding groups. Macrocyclic ligands provide one means of doing this. The often arduous synthesis of macrocycles, however, will restrict most future applications of them. Suitable designed hexadentate tripodal ligands ("supertripods", a subclass of podands) combine the high binding affinity of macrocycles with ease of synthesis. In addition, supertripods lend themselves naturally to practical applications through, e.g., incorporation into polymers. The talk will describe the synthesis and coordination chemistry of supertripodal ligands as chelating agents for a variety of transition metal ions, and conclude with a view to possible applications.

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CHEMISTRY OF CROWN THIOETHER COMPLEXES OF LOW-VALENT SECOND-ROW TRANSITION METALS

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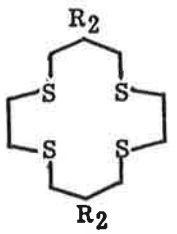
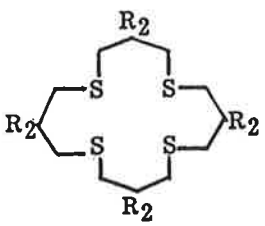
Recent studies on transition metal complexes of crown thioethers are inaugurating a new era for the thioether coordination chemistry. To date most researches, however, have devoted to synthesize the complexes exhibiting unusual structures and static properties, and their reactivities yet remain to be elucidated.

We present the preparation, structures, and reactions of 14- and 16-membered quadridentate crown thioether complexes, trans-$Mo(N_2)_2Me_8[16]$-$aneS_4$, cis- and trans-$RuCl_2L$, and RhL^+ (L=$R_4[14]aneS_4$, $R_8[16]aneS_4$; R= H, Me) together with the factors determining their reactivities. The most



$R_4[14]aneS_4$(R=H,Me)



$R_8[16]aneS_4$(R=H,Me)

prominent electronic property of the crown thioethers, which differs from that of phosphines, is p_π donor ability. Thus, trans-$Mo(N_2)_2Me_8[16]aneS_4$ and RhL^+ are more electron rich than the corresponding phosphine analogues. Typical reactions demonstrating the high nucleophilicity may be the unprecedented N-arylation and -benzylation of the coordinated N_2 ligand in the Mo(0) complex with RX (R=Ar, $PhCH_2$) and the facile oxidative addition of CH_2Cl_2 to the Rh(I) compounds. The nucleophilicity is also affected by the ring size and conformations of the macrocycles. These stereoelectronic effects will be discussed on the basis of molecular mechanics and extended Hückel MO calculations.

Two geometrical isomers of the Ru(II) complexes show a remarkable reactivity difference toward $C(sp^2)$-H activation; a reaction of cis-$RuCl_2$-$R_4[14]aneS_4$ with Al_2Me_6 in aromatic hydrocarbons gave trans-RuAr(Cl)-$R_4[14]aneS_4$, while the trans-isomer afforded an expected methyl complex. The ring size effect observed for the reaction of the Ru(II) complexes with $NaBH_4$ will be also presented.

PHOTOCHEMICAL C–H BOND ACTIVATION : NMR, MATRIX AND LASER KINETIC STUDIES

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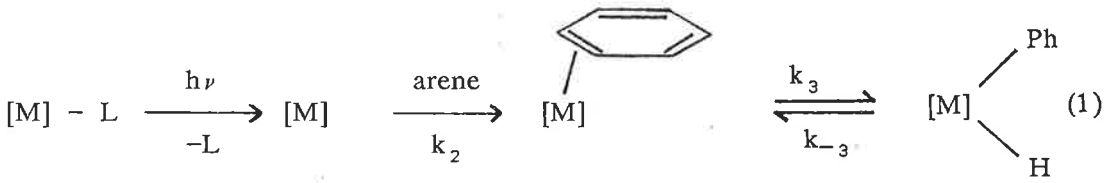
Many C–H bond activation reactions are initiated photochemically, making them suitable for kinetic investigations by laser flash photolysis and matrix isolation. When combined with information from conventional NMR studies, a detailed reaction mechanism may be built up. Examples of molecules under study include $CpRh(CO)_2$, $CpRh(PMe_3)(C_2H_4)$ and $(\eta^6\text{–}C_6H_6)Os(CO)(C_2H_4)$ (Cp $=\eta^5\text{–}C_5H_5$).

(a) Arene Activation The typical mechanism of photochemical arene activation involves three stages, generation of a coordinatively unsaturated intermediate, η^2–coordination of the arene, and C–H insertion [1]:



Studies of fluxional rearrangements of (phenyl)hydride complexes provide estimates of the barrier corresponding to process k_{-3}. Kinetic studies of $CpRh(PMe_3)(C_2H_4)$ by laser flash photolysis in benzene result in the detection of an intermediate which decays with first order kinetics (ca. 700 s^{-1} at 295 K). The same intermediate may be generated by photolysis of $CpRh(PMe_3)(\eta^2\text{–}C_6F_6)$ in benzene (see below). These and further observations lead to the identification of the transient as $CpRh(PMe_3)(\eta^2\text{–}C_6H_6)$. The temperature dependence for the conversion from (η^2–arene) to (phenyl)hydride complex gives activation parameters for the second process.

By using C_6F_6, the reaction of $CpRh(PMe_3)(C_2H_4)$ with arene may be arrested at the (η^2–arene) stage and the product characterized by NMR and X–ray crystallography. The product $CpRh(PMe_3)(\eta^2\text{–}C_6F_6)$ is stereochemically rigid, indicating considerable stabilization of the η^2–complex. By suitable choice of fluorinated arene, both coordinated arene and aryl hydride may be observed in a single system.

(b) Ethene Activation Photochemical isomerisation of ethene complexes to metal(vinyl)hydrides was recognized only recently [2]. Such isomerisations may be identified in matrix experiments by the characteristic vibrations of the vinyl group of the product. It is intriguing that $CpRh(PMe_3)(C_2H_4)$ undergoes such an isomerization in a matrix, but as yet no corresponding evidence has been obtained in solution. A further example is provided by $(\eta^6\text{–}C_6H_6)Os(CO)(C_2H_4)$.

(c) Coordinatively Unsaturated Intermediates

Most mechanisms proposed for C–H activation involve coordinatively unsaturated intermediates ([M] in eq. 1). Such species have proved too reactive to observe directly in solution, but may be observed in argon matrices, e.g. $(\eta^6\text{–}C_6H_6)OsCO$ from $(\eta^6\text{–}C_6H_6)Os(CO)(H)_2$.

1. W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 1984, 106, 1650.

2. D.M. Haddleton and R.N. Perutz, J. Chem. Soc., Chem. Commun. 1984, 1734 ; M.V. Baker and L.D. Field, J. Am. Chem. Soc. 1986, 7436,

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INFLUENCE OF CONFORMATION UPON RATES OF ELECTRON TRANSFER IN SOLUTION.

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Photoinduced electron transfer processes can occur on timescales ranging from about 10^{13} to 10^{-2} s^{-1}, according to the nature of the reactants and the environment. The observed rate of electron transfer depends critically upon a number of factors, including the mutual orientation of the reactants, and electron transfer can occur between partners which are spatially separate. In extreme cases, the rate of electron transfer can exceed the rate of conformational changes occurring in covalently-linked donor-acceptor complexes such that the redox act becomes selective. This situation has been investigated using a series of porphyrins containing different numbers and types of appended viologens. In all cases, the connecting bridge is a fexible hydrocarbon chain so that the resultant complex can exist in solution in a wide distribution of conformations.

Photophysical properties have been determined for the various porphyrin-viologen complexes in fluid solution using time-resolved fluorescence and laser flash photolysis techniques. Rates and yields of electron transfer processes have been derived from these studies. Redox properties have been measured by cyclic and differential pulse voltammetry methods and employed to estimate thermodynamic driving forces for the various electron transfer steps. Preferred conformations adopted by the porphyrin-viologen complexes have been probed by solution phase nmr and detailed computational studies.

The measured rates of electron transfer have been correlated with the anticipated structures of the complexes after correction for any fluctuations in thermodynamic properties. The orientational requirements for rapid electron transfer in such flexible systems are extrapolated from the data and will be described. The ability of the solvent to modulate the conformational distribution will be considered.

THE COORDINATION OF π-CONJUGATED BIDENTATE LIGANDS

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At issue is a study of symmetry controlled interactions between the d-orbitals of a central transition-metal ion and the π-orbitals of a conjugated macrocyclic ligand. In an introductory theoretical part, it is shown how these interactions can be incorporated in existing Ligand Field theories. The result is a general model, capable of describing the coordination of an arbitrary number of π-conjugated bidentate ligands in any desired coordination geometry. This model is then applied to existing bischelate and trischelate complexes, for which detailed spectral and magnetic data are available. In a third part an account will be given of new detailed experimental evidence, recently obtained at the Universities of Leuven and Louvain-La-Neuve (1). The new data include the low-temperature single crystal ESR spectra of a tetra-imine macrocyclic Co(II) complex, $[Co(C_{10}H_{20}N_8)]Cl_{12}$, diluted in the analogous Ni(II) complex, and the corresponding crystal structures. The g-factor anisotropy and superhyperfine interactions in this complex, in combination with earlier data on β-disubstituted bischelated complexes, provide a conclusive proof for the existence of symmetry-controlled interactions between the metal d-orbitals and the π-orbitals of macrocyclic ligands.

(1) A Ceulemans, R Debuyst, F Dejehet, GSD King, M Vanhecke, LG Vanquickenborne, submitted for publication.

CALCULATION OF NMR CHEMICAL SHIFTS OF INORGANIC COMPOUNDS BY EMPIRICAL MOLECULAR ORBITAL METHODS

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NMR has become a useful tool in the research of structure and bonding in inorganic chemistry. Their numerical calculation may be achieved by two paths. One is the Sum-over-states pertubation theory (SOS) based on Ramsey's theory and developed by Schlichter. Another is the finite pertubation theory (FPT) developed by Karplus, Lipscomb, Ditchfield, Pople and Ellis' groups. Recently, we have developed the MNDO/GIAO method to calculate C-13, N-15 and O-17 NMR chemical shifts for a set of typical simple compounds. Most of these methods have been used to calculate the chemical shifts of simple compounds with only s and p orbitals. It is evident, therefore, that approximate methods including d and f orbitals should be developed for inorganic and organometallic compounds.

Fenske et al. have developed for the first time a quantum mechanical expression for the NMR chemical shifts via the X_α-SW method. The Fenske-Hall MO model is also extended to calculate the NMR chemical shifts for these complexes. It can perdict the C-13 exprerimantal trend with less computer time.

On the basis of the formulas and integrals which we have deduced for the INDO-SOS approximation, a program has been designed, to include d and f orbitals. An INDO-FPT semiempirical scheme extended by us seems to be attractive, which can be used not only in a simple way but also accurately to elucidate experimental facts for complexes (Table). There is also a good linear relationship between the calculated

Table: C-13 Chemical Shifts of $(\eta^5\text{-}C_5H_4)_2Fe(CHO)_2$ (ppm)

	ρ_s	σ^d	σ^p	σ_{cal}	σ_{exp}
C_1	0.1053	56.93	-120.22	-63.30	-80.10
C_2	0.0707	57.18	-120.31	-63.13	-74.05
C_3	0.0539	57.30	-119.06	-61.76	-70.75
C_4	0.3598	54.98	-231.66	-176.68	-192.71

σ^d_{cal} and electronic charge ρ_c on the carbon atoms.

Most of our calculation give experimentally observed trends in the chemical shifts and provide some useful qualitative results.

1. D.F.Freier, R.F.Fenske and You Xiao-zeng, J.Chem.Phys. 83, 3526 (1985), Chem.J. of Chinese Univ., 30, 1253 (1987).
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ASPECTS OF AROMATIC IRON SANDWICHES : APPLICATIONS TO ORGANIC SYNTHESIS, CATALYSIS AND MOLECULAR MATERIALS.

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The ability of transition metal sandwich complexes to transfer electron(s) is a predominant feature of their chemistry[1]. This characteristic can be used or, on the contrary, avoided, depending on the specific problem addressed. New modes of activation using 17, 19 and 20-electron iron sandwiches have been disclosed using such electron-transfer pathways.

In some other instances, the powerful activation by organo-iron cationic moieties follows pairwise schemes and must avoid side electron-transfer paths[2]. Strategies will be described on this line to make modified ligands including discoid molecules[3].

Finally, the use of iron-sandwich complexes as catalysts in electron-transfer chain reactions is shown with emphasis on the coupling with organometallic catalysis[4].

1. Connelly, NG; Geiger, WE, Adv. Organomet. Chem. 1985, 25, 87.
2. Astruc, D; Michaud, P; Madonik, AM; Saillard, J-Y; Hoffmann, R, Nouv. J. Chim. 1985, 42, 41.
3. Moulines, F; Astruc, D, Angew. Chem. Int. Ed. Engl. 1988, 27, 1347.
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New Findings in the Arene Chemistry of the 3d Transition Metals

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In our recent account on *Reactive Organometallic Compounds Obtained from Metallocenes and Related Compounds* [1] we mentioned a series of dinuclear 3d transition metal complexes with monocyclic arenes as bridging ligands. Among the compounds considered was the divanadium complex $(CpV)_2C_6H_6$, which is the first triple–decker sandwich complex having complexed benzene as the *middle deck.*

This lecture surveys new results on the ligand properties of the bicyclic naphthalene molecule. Aspects to be covered include:

1) The synthesis and properties of mononuclear complexes having η^2–, η^4– or η^6–bonded naphthalene. Examples of complexes of the latter type are $CpM(C_{10}H_8)$ (M = Cr, V). Because of the facile displacement of the η^6–bonded naphthalene (*naphthalene–effect*) both these complexes are valuable sources of CpM fragments for synthesis.

2) The two step preparation of cyclopentadienylbenzocyclohexadienyliron and its monodeuterated derivative starting from ferrocene. $CpFe(C_{10}H_8–H)$ and $CpFe(C_{10}H_8–D)$, which can be regarded as a naphthalene molecule hydro– or deuterometallated by CpFeH(D) fragments, undergo the *retro*–hydro(deutero)metallation, liberating the naphthalene very easily. Thus these new compounds are ready sources of CpFe fragments with metal–H or metal–D bonds.

3) The syntheses and structures of homo– and heterodinuclear complexes in which the naphthalene molecule functions as a bridging ligand.

1. K. Jonas, Angew. Chem. Int. Ed. Engl., 1985, 24, 295.