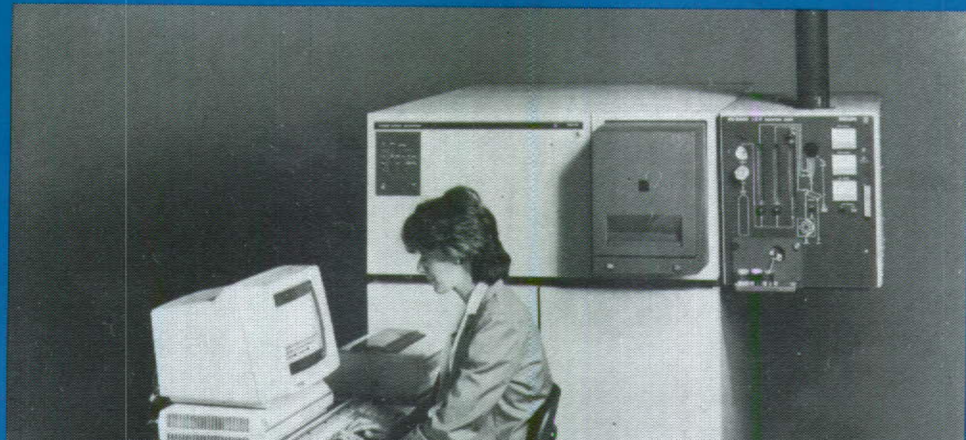
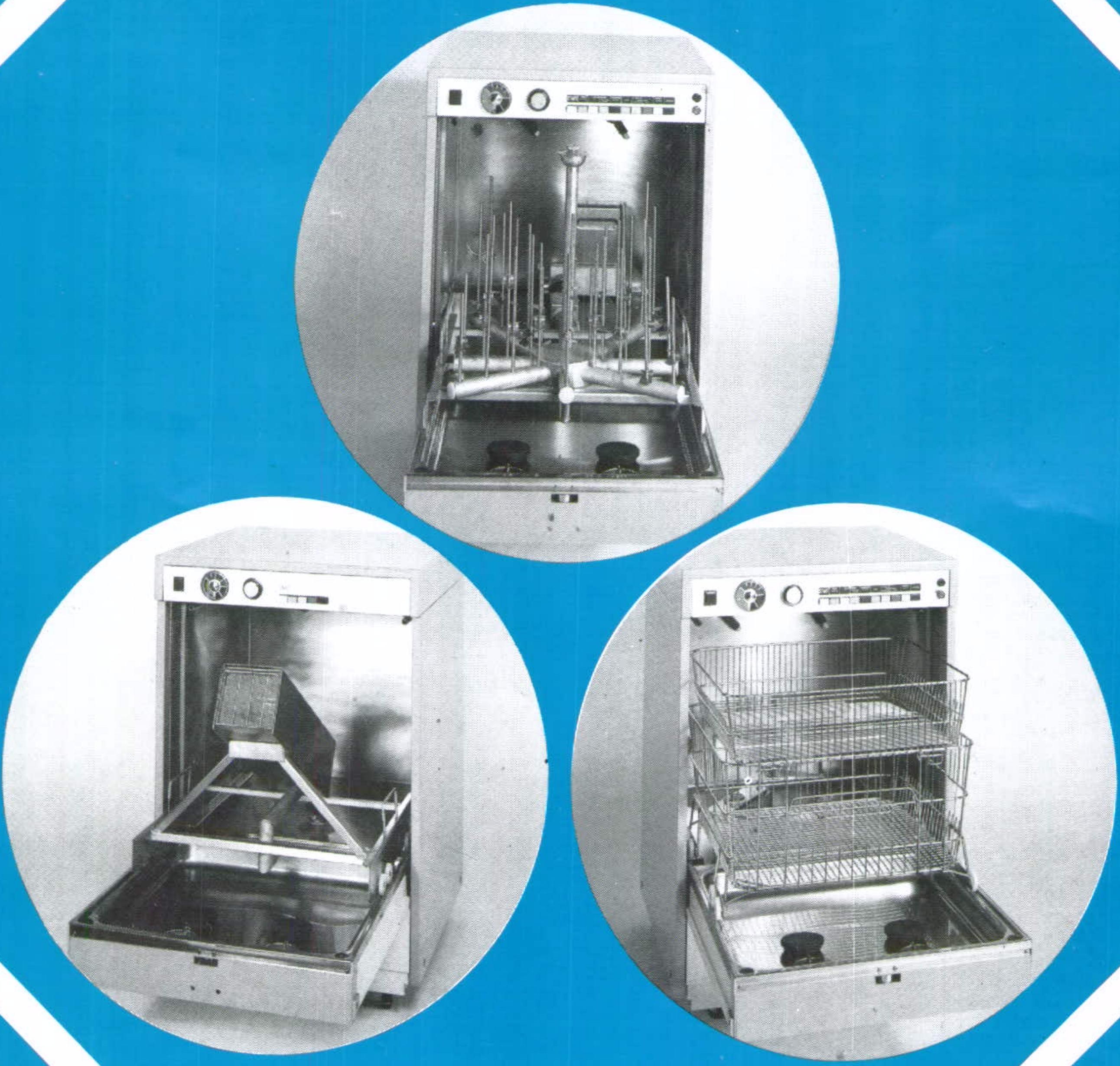
December 1984 Volume 48 No. 7

Chemistry in new zealand





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Chemistry in new zealand

Chemistry in new zealand

Philips launches high-performance optical emission range.

Scientific & Industrial Equipment

PHILIPS

FRONT COVER STORY: PAGE 174

Philips launches high-performance optical emission range

The PV 8050 Series of optical emission spectrometers from Philips Analytical is available in a choice of configurations optimised for different applications of conventional electrical discharge and inductively coupled plasma excitation.

All are microprocessor-controlled, and can be used with either DEC or Hewlett Packard computers for data processing.

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EDITORIAL

In this issue we look at organometallic chemistry, and the related area of catalysis. The feature articles review work on organometallic chemistry at the universities of Auckland, Waikato, and Otago. In the first instance this is purely academic research, but hopefully its interest extends beyond that narrow sphere. The work of Warren Roper has received international acclaim. That at Otago and Waikato has been considered of sufficient potential for the petroleum industry to receive funding from both local and international organisations. I must confess to a personal bias, through prior association, but I trust the rest of you will also find some interest in this work.

The strong academic bias of this issue highlights what is probably an eternal editorial dilemma. The academics will possible see this as a good move; the non-academics may start to wonder about withdrawing their subscriptions. (Interestingly, there are people from outside the goldfish bowl who would see us all as academics). Rest assured, we shall continue to aim to provide a balance of articles, reflecting the diverse interests of the members of this Institute. In this regard though one might consider a few simple calculations: The Journal is now approaching its fifieth year. If we maintain the present rate of publication, in the next fifty years there should be three hundred issues with ten to twelve pages in each devoted to members' articles. In fact, if we ignore membership change, about two pages per member. Hmm! Are you getting your share?

Bruce Graham

PEOPLE

INSTITUTE PRIZES — 1984

Shell Industrial Chemistry Prize

John Ayers, Reader at Massey University, has been awarded the 1984 Shell Industrial Chemistry Prize for his work with cellulosic ion exchange resins. He developed these ion exchangers at Massey University with a view to their being used for the large scale recovery or purification of proteins and they are now being manufactured successfully by Waitaki NZ Refrigerating Ltd under licence agreements.

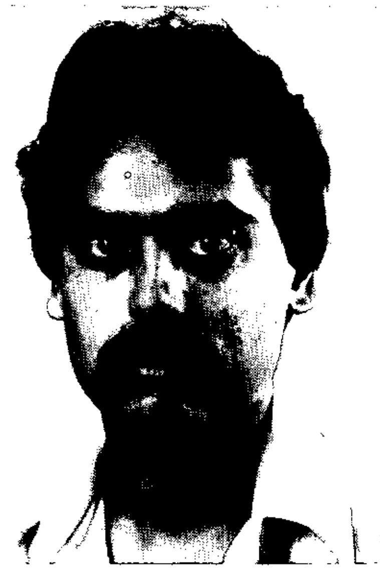
John is a graduate of the University of Canterbury, completing first a B.Sc.(Hons) and then a Ph.D. in 1968 on organophosphorus reaction mechanisms. He then went to the USA to work with lignin model compounds and pollution problems arising from the pulp and paper industry. Since taking up a lectureship in 1971 in the Department of Chemistry, Biochemistry and Biophysics at Massey University he has continued to take an interest in the industrial application of Chemistry. In the early 1970's he helped Tasman Vaccine Laboratories with the Grant Resins being investigated for use in recovering protein from the effluent of meat works. When this work proved to be unsuccessful he continued to develop his own range of cellulose derivatives for a variety of applications such as; the specific binding of the cholesterol carrying lipoproteins in serum; the recovery of proteins from whey; enzyme purifications. It is some of these derivatives which are now in production.

John continues to be involved with several companies and research groups around New Zealand and in many cases is designing special resins for their needs.

Reminder: Entries for the 1985 ICI, Shell, and Chemical Essay awards close on 30 April, 1985. (For details consult the 1984 Yearbook. Entries should be sent to the Administrative Secretary, P.O. Box 29-183, Christchurch).

A.C. Kennett Memorial Award

Mr Tony Eaton has won the inaugural Arthur C. Kennett Memorial Award. The award, which is co-sponsored by the Australasian Corrosion Association and the NZIC, is given annually for the best paper submitted on non-metallic corrosion. Mr Eaton has been a technician in the Auckland branch of Chemistry Division, DSIR, since 1978, and has spent much of that time, very appropriately, working with the late Mr Kennett on various topics in applied chemistry. His award-winning paper was entitled "Degradation of polyethylene film in contact with calcium hypochlorite".



VISIT OF DR ANNE DELL

Dr Anne Dell, Lecturer in the Biochemistry Department at Imperial College, London, England, visited research centres in the North Island during 6 - 11 September. She had presented a Plenary Lecture to the 9th Conference of the Australian and New Zealand Society for Mass Spectrometry, held at the Australian National University in Canberra during 27 - 31 August. Dr Dell is well known for her work on the structural analysis of high molecular weight compounds by fast atom bombardment (FAB) and field desorption mass spectrometry. In New Zealand there are now two mass spectrometers that are fitted with FAB sources, namely those at Massey University (Professor R. Hodges) and at Ruakura (Dr P. Holland). As this method of analysis by mass spectrometry is a very recent and important addition to this country's research expertise, the visit of Dr Dell at this time was most opportune. Travel assistance was provided by the Institute and by the New Zealand Branch of the A.N.Z.S.M.S.

While in New Zealand, Dr Dell addressed seminars in Wellington, Palmerston North and Hamilton on the subject: "Applications of Fast Atom Bombardment Mass Spectrometry to the Analysis of High Molecular Weight Biopolymers". Biological polymers (proteins, carbohydrates etc.) are not readily analysed by conventional mass spectrometry, in which ionisation takes place in the gaseous phase, as they are usually involatile and thermally unstable. In a fast atom bombardment source, ionisation takes place on the surface of a liquid. The compound to be analysed is dissolved in glycerol, or in thioglycerol for less polar molecules, and bombarded by a stream of rapidly moving argon or xenon atoms. The compounds on the surface ionise and the ions sputter into the gas phase where they are analysed by the application of electric and/or magnetic fields in the usual manner. This system can be retrofitted to current mass spectrometers relatively cheaply. However, high field magnets (that are very expensive) have been developed for the analysis of ions of high mass at full sensitivity from compounds of very high molecular weight.

Dr Dell described how this method of analysis has been applied to a variety of proteins, carbohydrates and other natural products. She showed how it could be used for the mapping of recombinant DNA protein products to discover errors in cloning. This requires experience in both mass spectrometry and protein biochemistry.

INDUSTRIAL

Dr K.G. Town has moved to Chem Industries from BP Laboratory, Petone. In his new position he is Quality Assurance Manager, and chief technical adviser in the field of contract manufacturing of pharmaceutical cosmetics and toiletries.

Cheryl Smith moved to Cerebos Foods from Johnson Wax in October, taking up the position of Food Technologist for product development.

Mr Simon Monks has left Chem Industries to take up the position of Technical Manager with Johnson and Johnson.

Dr Peter Bailey of Flinders Cook (Technical Services) Ltd advises that his laboratory is now operating from new premises at 3 Fenton St, Mt Eden, Auckland. This represents a move to bigger, better facilities, and Peter assures us that the same can be said of the services he provides. The phone number, postal address and telex number are unchanged.

In Dunedin, **Dr Warren Bryson** has recently opened an analytical laboratory and consultancy (Scientific Analytical Ltd.) at which he intends to carry out testing for local Industry and farm advisers. He is currently carrying out herbage analysis using atomic absorption spectroscopy.

From the Aluminium Smelter at Tiwai Point, **Mr John Wallaart** reports that new Mettler automatic sampling and titration equipment has been installed in the Chemistry Laboratory. This is to be used as a back-up system for product analysis in the event of a failure of the X-ray spectrometer usually used to monitor product quality. New staff at the Smelter include **Miss Rona MacArthur,** a chemistry graduate from the Victoria University of Wellington, and laboratory assistant, **Miss Debbie Smith.**

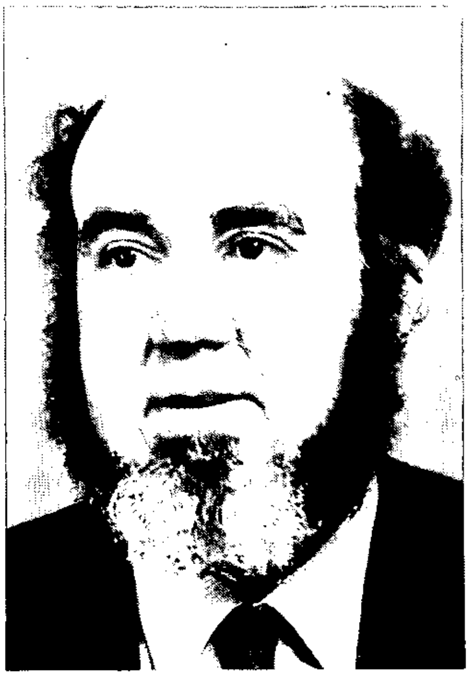
John Kenny, from the Southland Co-operative Phosphate Co., Awarua, reports that Technical Manager, **Stan Winter** will attend the Australian Fertiliser Industry Technical Conference in Perth in November as one of the representatives of the N.Z. Fertiliser Industry. Also, the Awarua Works hosted a meeting of the FMRA Technical Process Committee in August. The principal purpose of this meeting was to organise the FMRA's 9th Research Symposium to be held at the Bay of Plenty Co-op Fertiliser Co. at Mount Manganui in February. This symposium will be concerned primarily with quality control.

Bruce Collier reports that N.Z. Cement Holdings Ltd. have recently purchased a J.A.F. conduction calorimeter for the laboratory at Burnside (Dunedin) in order to make measurements of heat of hydration characteristics during the setting of their cement. Such measurements are particularly important in "mass concrete" projects where heat build-up during the first three days after pouring, and subsequent shrinkage, can cause cracks. Conduction calorimetry gives more-meaningful information than heat-of-solution methods.

MULTIPLE BONDS BETWEEN TRANSITION METALS AND CARBON — RECENT ORGANOMETALLIC STUDIES AT AUCKLAND

W.R. Roper,
Chemistry Dept, University of Auckland.

Warren Roper is a graduate of the University of Canterbury, and has been on the staff at Auckland since 1966. Warren is this year's recipient of the ICI prize awarded by the Institute. Other recent successes include the 1983 Royal Society of Chemistry Award for Organometallic Chemistry, Fellow of the Royal Society of New Zealand, and the appointment to a Personal Chair at Auckland. It is indeed a pleasure to be able to present this review of Warren's research activities. — Ed.

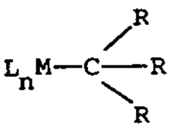


Abstract

The functional groups $>C=C<$, $-C\equiv C-$, $>C=N-$, $-C\equiv N$ and $>C=O$, all involving carbon in multiple bond formation to a first-row element, are very familiar to organic chemists. Recent studies have shown that carbon can also form multiple bonds to second-row p-block elements, e.g., $>Si=C<$, $-P=C<$ and $P\equiv C-$ and even to transition metals, $M=C<$ and $M\equiv C-$. This article summarizes the findings of recent research at the University of Auckland on stable molecules with the following linkages, $L_nM = CH_2$, $L_nM = CF_2$, $L_nM = CCl_2$ and $L_nM\equiv CR$. It is shown that in understanding the chemistry of these new molecules it is helpful to think of the $M=C<$ and $M\equiv C-$ bonds as being "alkene-like" and "alkyne-like", respectively. Molecules with multiple metal-carbon bonds are not just intriguing structural curiosities but represent a principal class of organometallic compounds. Furthermore, compounds of this type are key intermediates in the catalysis of industrially important reactions, such as alkene metathesis, and increasingly are used as intermediates for organic synthesis.

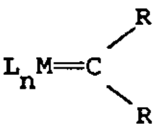
Introduction

A chemist, of any particular persuasion, asked to name a typical organometallic molecule, would probably choose ferrocene, $Fe(\eta^5-C_5H_5)_2$, or some related π-complex in which an assembly of carbon atoms is symmetrically, or more or less symmetrically, bound to a metal atom. However, many organometallic molecules have ligands in which only one carbon atom is bound to the metal and if we restrict our attention to examples of this type we can recognize the following three bonding situations:



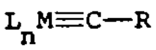
metal alkyl complex

1



metal carbene complex

2

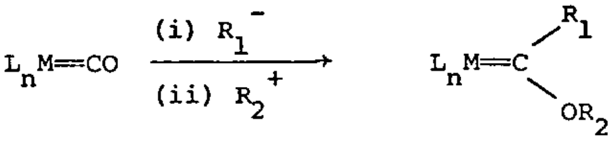


metal carbyne complex

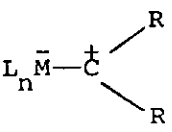
3

Inorganic chemists think of the molecules they study (even organometallic molecules) as being composed of "metal" and "ligands" and name molecules accordingly, hence bonding situations 2 and 3 are named after the free ligand fragments, CR_2 (carbene) and CR (carbyne), respectively. In our research at Auckland we have been interested in complexes of all of the above types, but this account deals only with the multiple bond situations depicted in 2 and 3.

The first transition metal carbene complex was prepared and characterised by Fischer and Maasböl in 1964.[1] The synthesis involved sequential nucleophilic and electrophilic addition to a metal carbonyl complex.



This approach obviously leads to a π-donating oxygen substituent on the carbene carbon atom and for nearly a decade following this initial discovery all carbene complexes reported had, O, N, or S heteroatom substituents. The stabilising effect of these heteroatoms has its origin in the π-donating ability of these substituents, a fact which is readily apparent from a simple consideration of the bonding in these complexes. Structural studies have invariably confirmed that the three bonds about the carbene carbon atoms lie in one plane and carbene complexes may therefore be viewed as metallated carbenium ions,



The empty p-orbital at the carbene carbon atom is perpendicular to the plane of the three σ-bonds and by π-interaction between the carbene carbon atom and its three substituents, electron-deficiency at the carbene carbon is reduc-

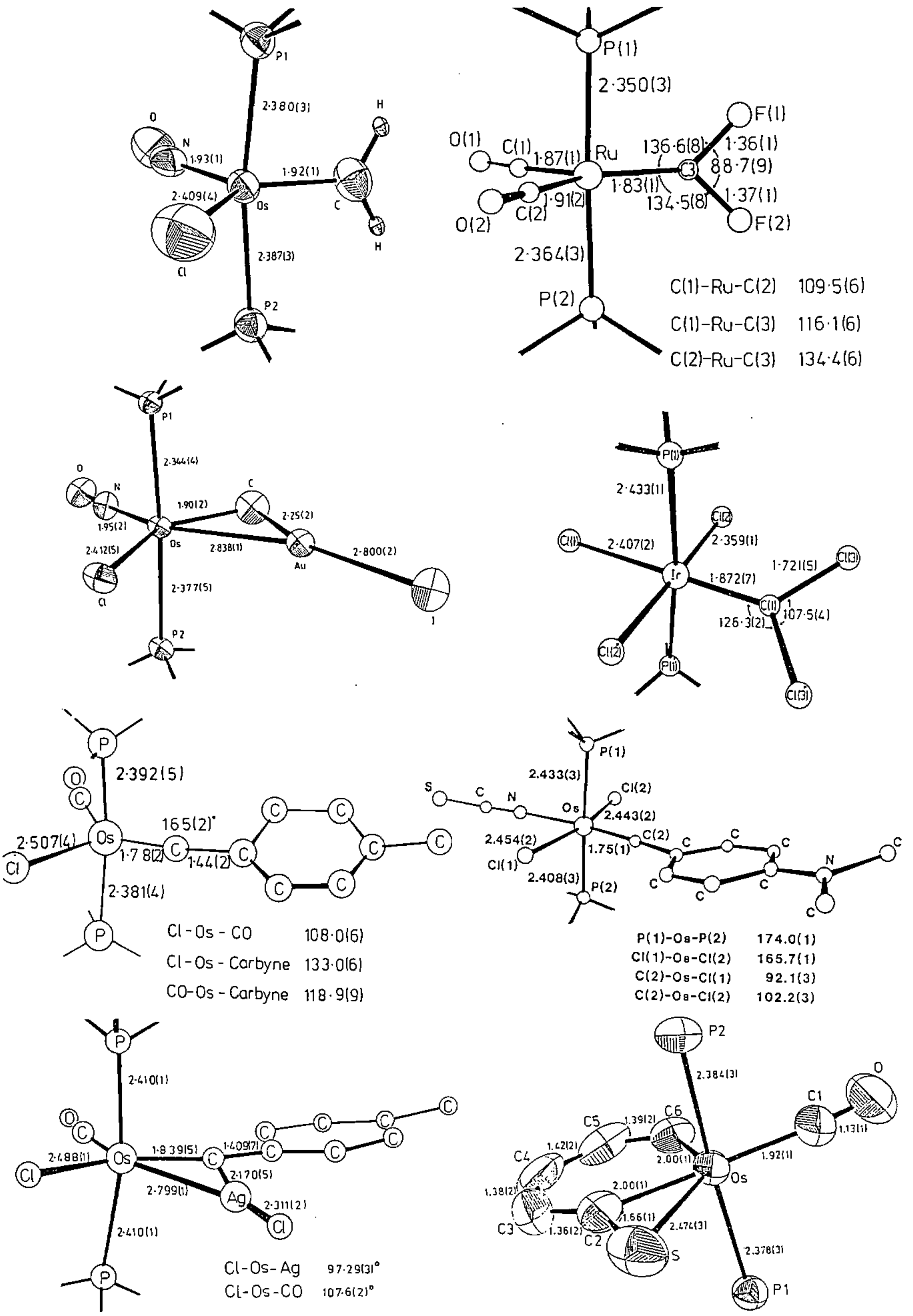
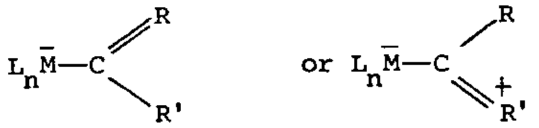
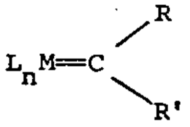


Figure 1. Structures of eight of the molecules discussed in the text. (In each case the phenyl rings of the *trans*-triphenylphosphine ligands have been omitted for clarity.)

ed. The stabilizing effect of O, N, S –substituents, which are π-donors, is obvious, and contributing valence bond structures.



may be written. Stable complexes without good donor heteroatom substituents, e.g. R = H, alkyl, aryl, halide, etc., must rely entirely on π-donation from the metal, i.e.,



Some examples of this type, with genuine metal-carbon double bonds, will now be described.

$L_nM = CH_2$

Early attempts to prepare terminal methylidene (CH_2) complexes, $L_nM = CH_2$ often led instead to $L_nM(CH_2=CH_2)$ or to $L_nM\overset{\diagup CH_2 \diagdown}{\text{———}}ML_n$. This was because available reaction pathways for an unprotected CH_2- ligand involve either a self-coupling reaction to form ethylene (which is retained as a ligand) or the trapping of $L_nM=CH_2$ by L_nM to give a CH_2- bridged species. For the successful isolation of a stable $L_nM = CH_2$ molecule, therefore, it is not enough to find an electron-rich fragment L_nM with donor and acceptor orbitals appropriate for matching-up with CH_2, one must also provide steric protection to prevent these alternative reactions.

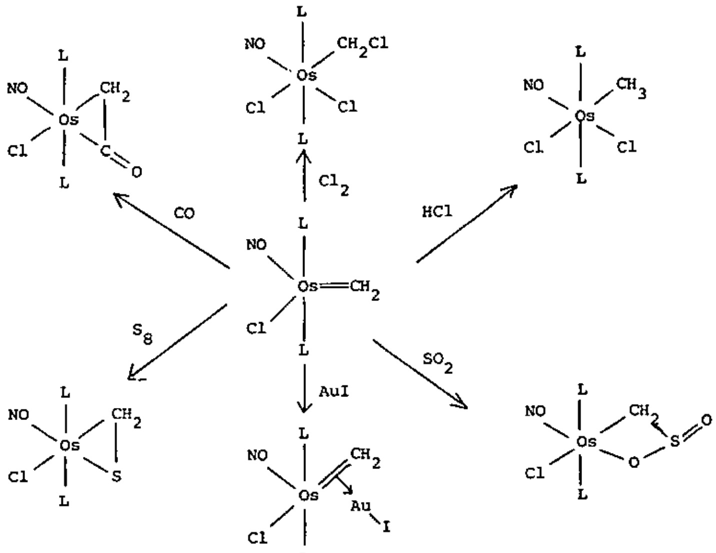
Exactly similar considerations apply to the isolation of compounds with Si = C and P = C bonds where very bulky substituents are used. Excellent steric protection of the CH_2- ligand is provided by two mutually ***trans*** triphenylphosphine ligands. It should be noted that ***all*** the molecules described in this account have a pair of ***trans*** triphenylphosphine ligands.

The CH_2- ligand can be introduced into a metal complex by using diazomethane as a reactant. An example which fulfills the requirements given above (electron-rich metal centre and steric protection) is

$$OsCl(NO)(PPh_3)_3 + CH_2N_2 \longrightarrow Os(=CH_2)Cl(NO)(PPh_3)_2 + N_2 + PPh_3$$

The resulting CH_2- complex,[2] $Os(=CH_2)Cl(NO)(PPh_3)_2$ is a high-melting (>200°C), air-stable, crystalline solid, the structure of which has been determined by single crystal X-ray diffraction and is depicted in Figure 1 along with the structures of several other molecules discussed herein. The observed Os-C distance is about 14 % less than the distance expected for an Os-C single bond and is compatible with a double bond. The orientation of the CH_2- ligand is that expected for maximum π-donor overlap from the metal.

Despite the substantial steric blockade, $Os(=CH_2)Cl(NO)(PPh_3)_2$ undergoes a number of reactions which reveal the alkene-like nature of the Os = C bond. In Scheme 1 is shown a selection of typical reactions. Addition reactions are exemplified by HCl and Cl_2, reaction with S_8 produces a thioformaldehyde complex (compare episulfide formation with an alkene), CO in a C-C bond-forming reaction gives a ketene complex, SO_2 gives a sulfene complex and finally the $Os = CH_2$ function is seen behaving as a ligand towards another metal centre in the reaction with AuI. The structure of this last complex is also shown in Figure 1 where it is depicted as a dimetallacyclopropane derivative. It is interesting to note that several of the ligands formed above, CH_2S, CH_2SO_2, and CH_2CO are very unstable as free molecules but the resulting complexes are quite stable.



Scheme 1 (L = PPh_3)

$L_nM = CF_2$

It is possible to introduce a CF_2- ligand into the same osmium substrate by using the reactive molecule, $Cd(CF_3)_2$, as the source of CF_2[3].

$$OsCl(NO)(PPh_3)_3 + Cd(CF_3)_2 \rightarrow Os(=CF_2)Cl(NO)(PPh_3)_2 + CF_3CdF.$$

Again, the structure is a trigonal bipyramid with ***trans*** triphenyl-phosphine ligands and the Os-C distance, while still appropriate for a double bond is a little longer than in $Os(=CH_2)Cl(NO)(PPh_3)_2$.

In general CF_2- complexes are accessible from trifluoromethyl complexes ***via*** fluoride abstraction with a suitable reagent.[4]

$$L_nM{-}CF_3 \longrightarrow L_nM = CF_2]^+ + F^-$$

Successful syntheses have employed SbF_5, anhydrous HCl gas, and Me_3SiCl as fluoride-removing reagents. The most frequently observed reaction of a CF_2-ligand (often unintentional!) is hydrolysis to a carbonyl ligand

$$L_nM = CF_2]^+ + H_2O \rightarrow L_nMCO]^+ + 2HF$$

although if the metal centre is sufficiently electron-rich (low oxidation state metal) the electrophilicity of the ligand is reduced and addition reactions become important, e.g.,

$$Ru(=CF_2)(CO)_2(PPh_3)_2 + HCl \longrightarrow Ru(CF_2H)Cl(CO)_2(PPh_3)_2$$

$L_nM = CCl_2$

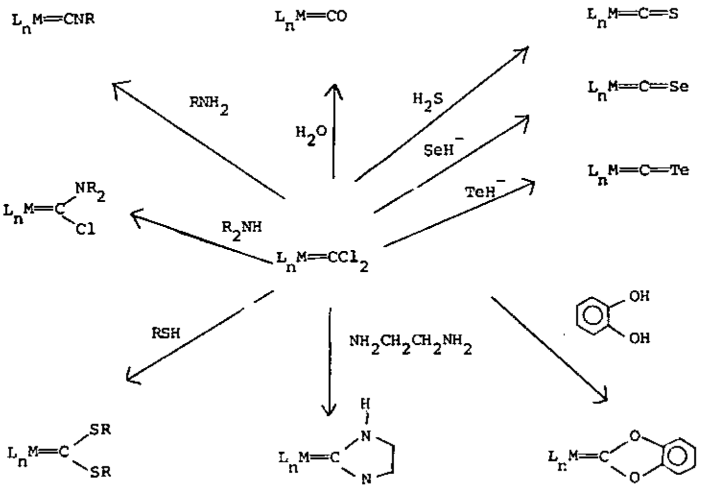
The first CCl_2- complex was reported in 1977.[5] We encountered an example in the same year from the reaction of $Ru(CO)(PPh_3)_3$ with CCl_4.

$$Ru(CO)(PPh_3)_3 + CCl_4 \rightarrow RuCl_2(=CCl_2)(CO)(PPh_3)_2 + PPh_3$$

Unfortunately, this reaction gave a variety of products and $RuCl_2(=CCl_2)(CO)(PPh_3)_2$ was formed in very low yield. However, recognition that CCl_2- complexes should be generally available from trichloromethyl precursors, e.g.,

$$L_nM - CCl_3 \rightarrow [L_nM = CCl_2]^+ Cl^- \text{ or } L_{n-1}ClM = CCl_2$$

led to the successful synthesis of a number of CCl_2- complexes[6] and the structure of a typical example, $Ir(=CCl_2)Cl_3(PPh_3)_2$,[7] is shown in Figure 1. The range of



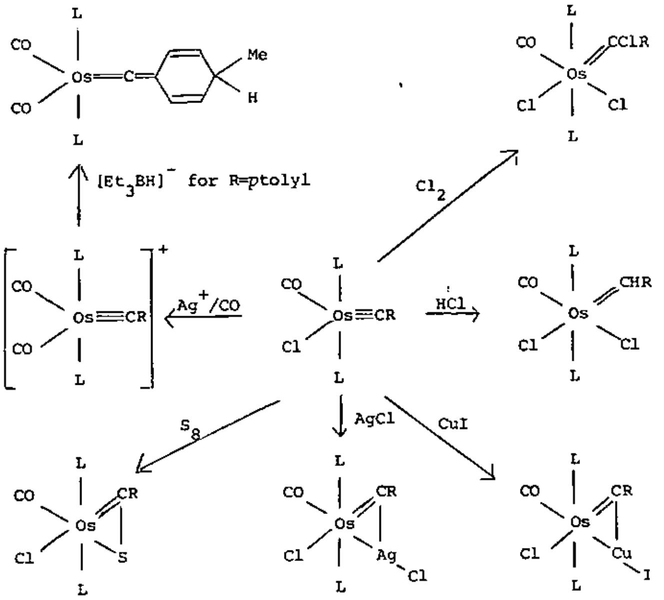
Scheme 2

known CCl_2– complexes should now expand rapidly with the discovery that CCl_3– derivatives result from reaction of CF_3– compounds with boron trichloride.[8]

$$L_nM{-}CF_3 + BCl_3 \rightarrow L_nM{-}CCl_3 + BF_3$$

The CF_3– derivatives are in turn prepared from readily available starting materials such as CF_3I, CF_3COCl, $Hg(CF_3)_2$ etc.

CCl_2– complexes are particularly interesting in that they combine an electrophilic carbene centre with the presence of carbene substituents which are good leaving-groups. The consequence is that these molecules very readily undergo substitution reactions in which CCl_2– ligands are converted into other carbene ligands.[9] Scheme 2 gives an indication of the range of possible reactions. In a sense we can compare the reactivity of $L_nM = CCl_2$ with the reactivity of phosgene, $O=CCl_2$. Among the unusual reaction products given in Scheme 2 we can note a tellurocarbonyl complex, $L_nM = C = Te$, the tellurium analogue of the ubiquitous carbonyl ligand. At the moment there is no other available route to CTe-complexes.[5]



Scheme 3 (L = PPh_3).

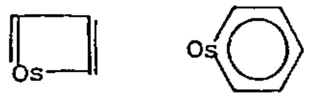
$L_nM \equiv CR$

In the last section it was emphasized that CCl_2– complexes undergo nucleophilic substitution reactions. When CCl_2– complexes react with lithium reagents, LiR, (where R is aromatic, e.g., phenyl, tolyl, etc.,) the result is the formation of metal-carbyne complexes[10]

$$L_nM{=}CCl_2 + 2LiR \longrightarrow L_nM{\equiv}CR + LiCl + RCl.$$

The first equivalent of LiR probably results in lithium-halogen exchange producing an intermediate CCl-complex which is then substituted by the second equivalent of LiR giving the observed CR-complex. The first step is effectively a reduction of the metal oxidation state by 2 units. The structure of a typical example, $Os(\equiv C\text{-}p\text{-tolyl})Cl(CO)(PPh_3)_2$ is shown in Figure 1. The very short Os—C distance is 20 % less than an expected Os—C single bond distance and is compatible with an Os≡C triple bond. Also, there is a very strong intra-red absorption at approx. 1300 cm^{-1} attributable mainly to ν(Os≡C). Again alkyne-like addition reactions characterize the chemistry of these molecules. In Scheme 3 we see that HCl, Cl_2, and S all "add" to the Os≡C bond. An attempted reaction with a nucleophile (H^-) carried out on the cationic carbyne complex, $[Os(\equiv CR)(CO)_2(PPh_3)_2]^+$, showed that the nucleophile avoided the carbyne carbon and added instead to the aromatic ring of the R-group producing a novel vinylidene complex.[11] The Os≡C bond functions as a ligand towards Cu(I), Ag(I) and Au(I) forming dimetallacyclopropene derivatives.[12] A related compound with a W≡C bond has been extensively used as a building block in very elaborate metal cluster syntheses.[13]

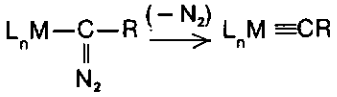
With the Os≡C bond established as an unsaturated entity it is possible to contemplate the use of this function in more ambitious syntheses. Cycloaddition reactions involving Os≡C together with one or two alkyne molecules could produce fascinating unsaturated metallacycles, a metallacyclobutadiene or a metallabenzene.



In fact, both of these possibilities have been realised[14],[15] and Figure 1 includes the structure of an "osmabenzene".

A further interesting reaction of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ involves oxidation of the metal centre by 2 units without interfering with the Os≡C bond. A typical oxidised product would be $Os(\equiv CR)Cl_3(PPh_3)_2$ and the structure of a derivative related to this is shown in Figure 1.[16] It can be seen that the Os≡C bond distance is only slightly changed by this oxidation.

Continuing development of M≡C triple bond chemistry will depend to some extent on improved and new methods of synthesis. One possibility we are presently exploring involves N_2 loss from an α-transition metal-substituted diazoalkane, [17] e.g.,



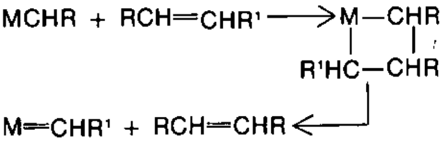
$$L_nM{-}\underset{\underset{N_2}{\|}}{C}{-}R \xrightarrow{(-N_2)} L_nM{\equiv}CR$$

Applications in Catalysis and Organic Synthesis

In the alkene (or olefin) metathesis reaction a catalyst rapidly establishes the equilibrium

$$2RCH{=}CHR' \rightleftharpoons RCH{=}CHR + R'CH{=}CHR'.$$

It is now known that the catalyst is a transition metal carbene complex (M=CHR) and the reaction consists of random, reversible formation of all possible metallacyclobutane rings as follows:[18]



$$MCHR + RCH{=}CHR' \longrightarrow \begin{array}{ccc} M & - & CHR \\ | & & | \\ R'HC & - & CHR \end{array}$$
$$M{=}CHR' + RCH{=}CHR \longleftarrow$$

An exactly similar metathesis of alkynes has been discovered using a transition metal carbyne complex as catalyst and proceeds through intermediate metallacyclobutadiene species.[19]

There are numerous instances of the use of transition metal carbene complexes in organic synthesis and a selection of reports from the recent literature will give a good indication of the diversity of applications and of the activity there is in this area. Carbene complexes have been used in the synthesis of cyclopropanes[20] (including enantioselective synthesis of cyclopropanes using chiral carbene complexes[21]), the synthesis of naphthoquinones[22] (including an extension to anthracyclines[23]), the synthesis of β-lactams, [24] and the synthesis of allenes.[25]

Conclusions

With $M=C$ and $M\equiv C$ now well-recognized functional groups the next goal for the synthetic inorganic chemist is to identify kinetically stabilised molecules with multiple bonds between transition metals and second and third row p-block elements. Already, species like $L_nM=PR$ have been established as intermediates in chemical reactions[26] and it must only be a matter of time before stable examples of these new bond types are forthcoming.

Acknowledgements

I am very grateful to my co-workers whose names appear in the references and especially to James Wright, Tony Wright and Simon Hoskins. My colleagues Joyce Waters, George Clark and Cliff Rickard gave indispensable assistance through providing crystal structure determinations.

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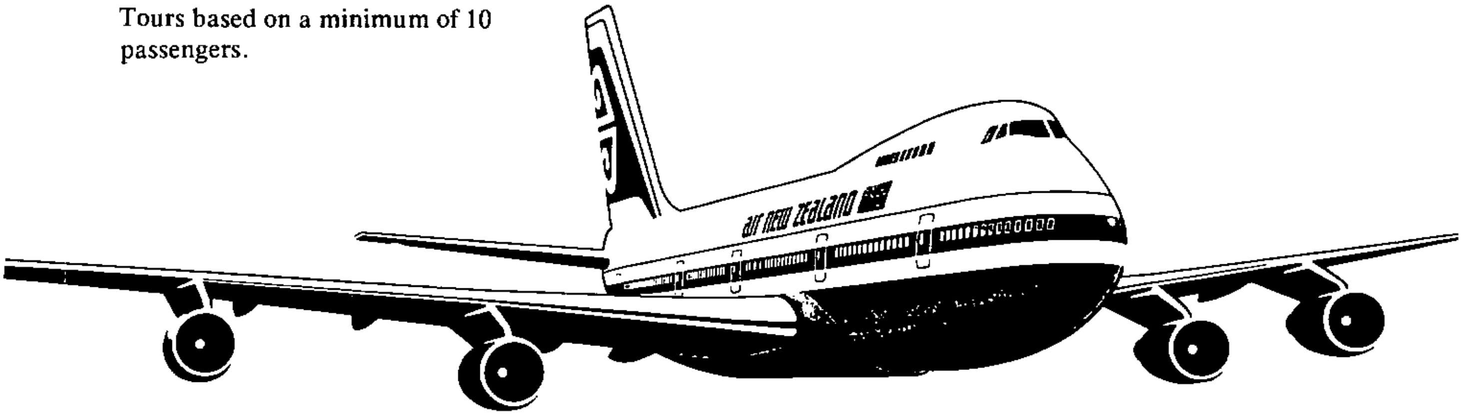

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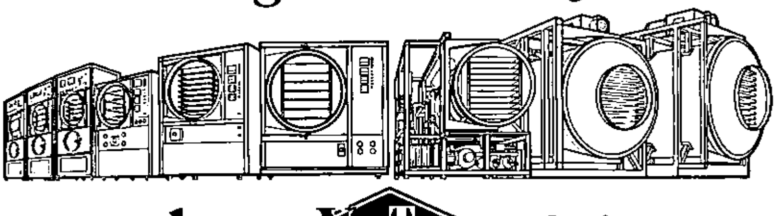

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ORGANOMETALLICS IN HOMOGENEOUS CATALYSIS: A NEW ZEALAND PERSPECTIVE

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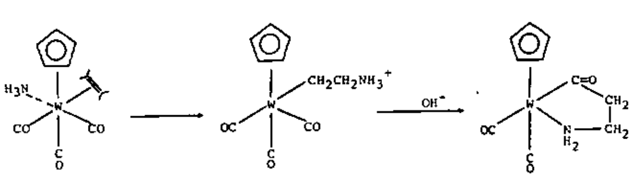
Jim Simpson graduated in Chemistry at the University of Southampton, B.Sc.(Hons) in 1964 and Ph.D. in 1967. After two years as a post-doctoral fellow at the University of Sussex he joined the staff at Otago where he is now Associate Professor. His current research interests lie in the fields of transition metal organometallic chemistry, organosilicon chemistry and X-ray crystallography.

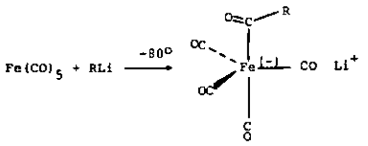
*After graduating Ph.D. in chemistry from the University of Canterbury in 1965, **Brian Robinson** gained post-doctoral experience at Newcastle-upon-Tyne and Manchester. He joined the staff at Otago in 1967 where he is now Professor and responsible for the Inorganic Section. Current research interests include the electron transfer and catalytic properties of metal clusters, chemical production from coal, and aspects of medical/inorganic chemistry.*

INTRODUCTION

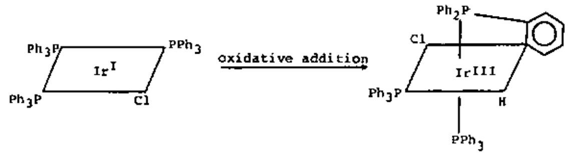
Almost every step in current and emerging technologies for the processing of energy resources to fuels and petrochemicals requires the use of specific catalysts. Most of the existing catalytic technology utilises *heterogeneous* catalysts, mainly metals and metal oxides. In many applications, their use is characterised by energy intensive, capital intensive processes with limited selectivity. The impetus for much of the industrial and academic organometallic research is the quest for *homogeneous* catalysts, which should offer milder reaction conditions, higher selectivity, easier product separation and reduced energy input. The function of the catalyst is to increase the rate of a thermodynamically allowed reaction by lowering the activation energy barrier for the process. In addition, if several reaction paths are allowed, the catalyst may increase product selectivity. Most organic molecules used as feedstocks, coordinate to low-valent metals and the formation of an organometallic compound can lower the activation energy barrier by bringing the reactants into close proximity on adjacent coordination sites,



making the organic molecule more susceptible to nucleophilic or electrophilic attack,



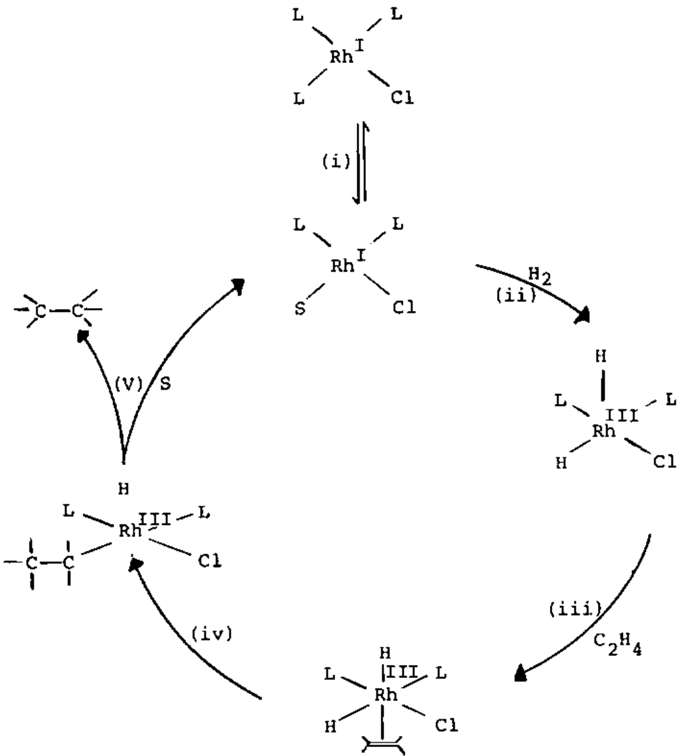
or providing low energy redox mechanisms.



Homogeneous catalytic cycles normally incorporate the creation of a coordinatively unsaturated centre, followed by a sequence of oxidative addition and/or 1,2-shift reactions.[1] For example, the catalytic hydrogenation of ethylene using rhodium(I) catalysts, Scheme 1, offers much greater selectivity, faster reaction rates, and the ability to carry out asymmetric synthesis.

Future catalytic developments should also permit the activation and utilisation of abundant resource chemicals such as CO_2, N_2 and coal.

Unlike Australia, New Zealand has not invested in catalytic research in its broadest sense. This could be short-sighted, as the sensible development of our most plentiful energy resource — coal — will necessitate an informed chemical body. This article examines some aspects of homogeneous catalytic research, deemed relevant to the New Zealand situation, which could profitably be carried out in this country, and details work currently in progress at the University of Otago involving electron transfer catalysis (ETC).

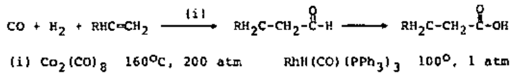


Scheme 1

(i) dissociation of L (e.g. PPh_3)
(ii) oxidative addition - formation of Rh-H
(iii) coordination of C_2H_4 cis- to Rh-H
(iv) 1,2 H-shift or 'insertion' of C_2H_4 into Rh-H bond, (mechanistically this is a migration of H to C_2H_4)
(v) reductive elimination - regeneration of the catalyst

AREAS OF RELEVANT RESEARCH

1. *C_1 CHEMISTRY.* There is a resurgence of interest in oxo chemistry and carbonylation reactions



$$CO + H_2 + RHC{=}CH_2 \xrightarrow{(i)} RH_2C{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}H \longrightarrow RH_2C{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH$$

(i) $Co_2(CO)_8$ 160°C, 200 atm $\quad$ $RhH(CO)(PPh_3)_3$ 100°, 1 atm

where new avenues have opened up for the catalytic conversion of CH_3OH to fuels. polymer precursors etc.[2] This body of technology is known as C_1 chemistry, reflecting the dependence on large scale synthesis gas ($CO + H_2$) generation from coal and/or natural gas.

Why the all-important reduction of CO by H_2 is catalysed in heterogeneous but not in homogeneous systems remains a chemical mystery and begs the question "is a metal surface necessary?" An understanding of this question is crucial, as homogeneous catalysts are effective in C_1 technology once this initial reduction step has occurred. Given an efficient reduction catalysis, one needs to control the chain termination step to halt at the appropriate C_n level; this can only be achieved by fine tuning a homogeneous catalyst.

2. *COAL CHEMISTRY.* Low-ranked coal, our most abundant energy resource, contains a high percentage of heteroatoms such as N and O. Coal-derived chemicals, making use of functional groups indigenous to the coal, would be valuable as a major, export earning, petrochemical operation, e.g. the conversion of hydrocarbons to functionally substituted products like vinyls or nitriles. It should be possible to devise catalysts for the cleavage of specific C-X bonds.

Bases such as Na_2CO_3 and $NaCO_2H$ catalyse the water gas reaction to produce heavy fuel oil. (Interestingly, soluble formates are considered to be the active reducing agents.) There is a need to determine whether our lignites contain sufficient basic material for this purpose, so that a combination of base reduction and catalysed hydrogenation (e.g. by $CO_2(CO)_8$ which could be recovered), would prove a feasible means of converting lignite to fuel oil.

An innovative attack would be to develop a small, mobile molecule which could tunnel into the coal and break down the matrix structure, an approach that would take advantage of the high permeability of the coal.

3. *HYDROCARBON ACTIVATION.* C-H bond activation in saturated alkane systems is not well established for soluble catalysts, except for non-specific electrophilic and free radical processes. Hydrocarbon activation is an area of major scientific challenge, as functionalisation would directly decrease hydrocarbon and energy consumption. Conceptually, alkane activation is possible through oxidative addition of C-H or C-C bonds to electron rich metal centres, or by electrophilic attack on the C-H bond by a metal centre to form a metal alkyl and a proton.

Both mechanisms have precedents in heterogeneous catalysis, but similar activation by organometallic complexes has only recently been discovered.[3]

ELECTRON TRANSFER CATALYSED (ETC) REACTIONS OF METAL CLUSTERS

In the field of catalysis, there is a two-fold interest in organometallic compounds containing two or more linked metal atoms[4] (collectively referred to as clusters for the purpose of this article). First, it is proposed, with some justification, that molecular metal clusters may provide reasonable models for the behaviour of metal surfaces.[5] In particular, clusters may mimic the way in which technologically important substrates such as H_2, CO and small organic molecules interact with the metal surface. Second, there is the expectation that clusters themselves may function as catalysts in homogeneous processes, at relatively low temperature and with much greater selectivity than their heterogeneous counterparts.[1]

One of the intrinsic difficulties with the use of metal carbonyl cluster compounds in catalysis is the kinetic stability of the coordinatively saturated molecules.[6] This problem is particularly relevant to the many 'catalytic' systems for which there is little likelihood that the integrity of the cluster unit is maintained throughout the catalytic process.[7] A potential strategy to circumvent this problem involves the use of odd-electron cluster systems, and work at Otago has concentrated on the chemistry of radical anions, produced by the chemical or electrochemical, one electron reduction of a variety of di- and trimetallic cluster substrates.[8 – 12]

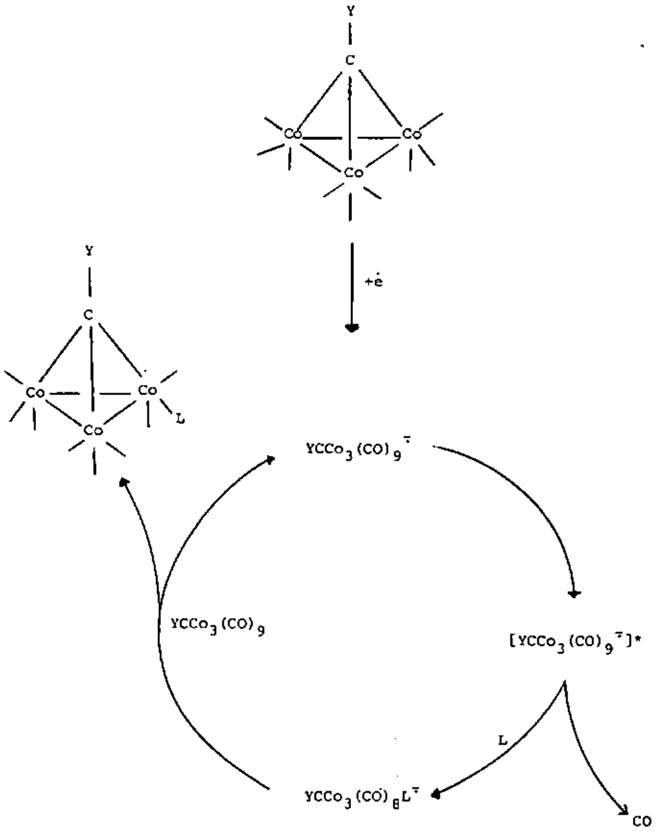
$$\text{CLUSTER} + e \leftrightarrow \text{CLUSTER}^{-\cdot}$$

The resulting radical anions are in most cases sufficiently persistent to allow an extensive investigation of their spectroscopic properties. Detailed analysis of the esr data for a range of radical anions reveals that the unpaired electron resides in an orbital that is primarily M-M antibonding in character. [13,14] The likely effect of radical anion formation is therefore to destabilise the cluster system and, in particular, to labilise the M-M bond(s) in the cluster framework.

Studies of the reactivity of these radical anions have shown them to be excellent substrates for electron-transfer catalysed (ETC) reactions which are typified by the catalytic substitution of coordination CO by alternative nucleophiles such as phosphines, arsines or nitriles.[15,16] A proposed ETC substitution mechanism is shown in Scheme 2.

The primary or initiation step is the reduction of the cluster to its radical anion, $YCCo_3(CO)_9^{-\cdot}$. Then follows a catalytic cycle in which the cluster radical anion forms an activated complex, $[YCCo_3(CO)_9^{-\cdot}]^*$, to provide a coordinatively unsaturated centre for attack by the entering nucleophile L. The formation of the radical anion of the substituted product $YCCo_3(CO)_8L^{-\cdot}$ leads to a kinetically fast and thermodynamically spontaneous electron transfer, from $YCCo_3(CO)_8L^{-\cdot}$ to a substrate cluster molecule, thus perpetuating the catalytic cycle.

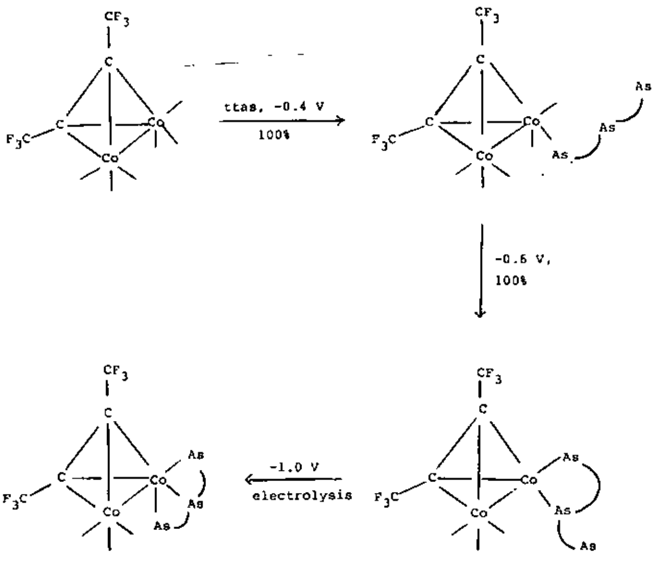
The reaction is truly catalytic, requiring only trace quantities of reductant (or very low Faraday/mol ratios) for initiation. Yields are significantly increased, temperatures lower,



Scheme 2

and reaction rates greatly increased (>10^6) compared to the equivalent thermal reactions.

Electrochemical generation of the initiating radical anion has significant advantages over chemical reduction in some cases, as it allows control of the potential of the reduction processes which, in turn, may effect the ultimate products from a given substitution process. For example, controlled potential electrolysis of the complex $(CF_3)_2C_2Co_2(CO)_6$ at −0.4V in the presence of the potentially tridentate ligand ttas, results in the high yield conversion to a substituted product with only one arsenic atom coordinated to cobalt, Scheme 3 If the electrolysis potential is decreased to −0.6V, a second catalytic step results in substitution by a second arsenic atom again in close to quantitative yield. The ultimate product with one cobalt atom chelated by all three donor atoms results from exhaustive electrolysis of the system at −1.0V. In contrast to the high degree of selectivity achieved by this controlled potential synthesis, the tris-chelate complex is the sole product of the equivalent thermal reaction under a wide variety of reaction conditions.[17]

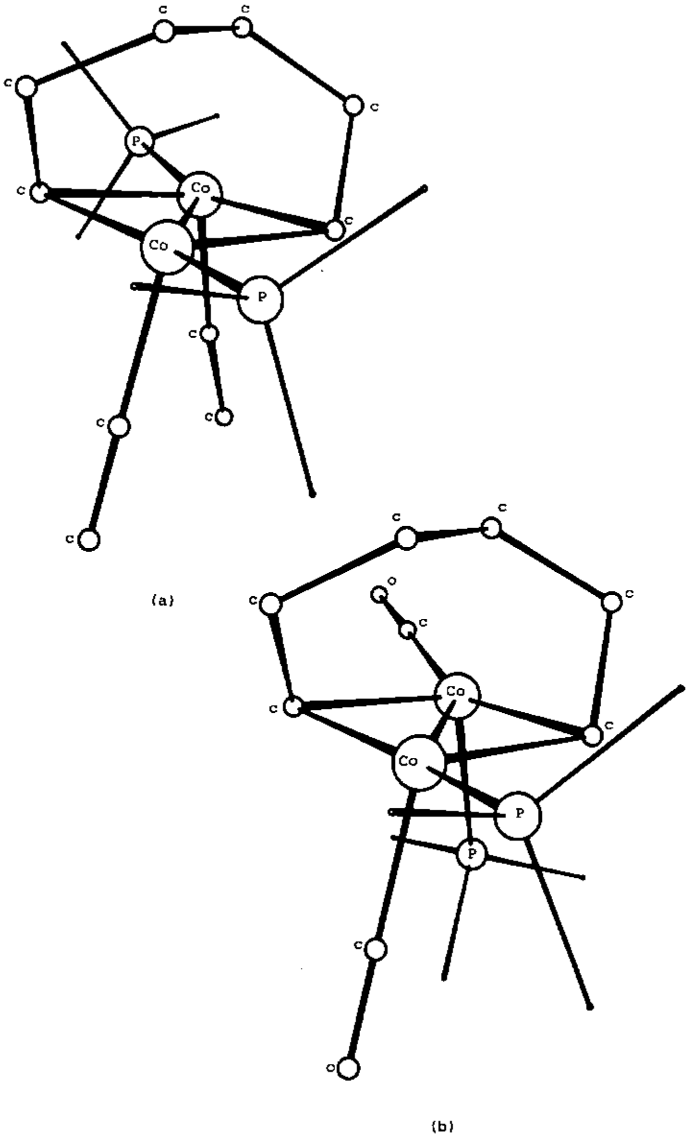


Scheme 3

A second category of ETC reaction is illustrated by a most spectacular catalytic isomerisation.[18] Attempts to electrolyse the blue solution of $(CF_3)_6C_6Co_2(CO)_2[P(OMe)_3]_2$ the sole product of thermal di-substitution of the 'flyover' complex $(CF_3)_6C_6Co_2(CO)_4$, results in an instantaneous colour change from blue to purple at the 'flick of a switch'. Crystallographic analysis of reactant and product from this unusual process reveals that the blue and purple compounds are in fact isomeric forms of $(CF_3)_6C_6Co_2$-$(CO)_2[P(OMe)_3]_2$, differing in the relative orientation of the phosphite ligands with respect to the backbone of the 'flyover' complex, Figure 1.

An isomerisation of this nature requires a significant reorganisation of the basic 'flyover' structure. The facility of transformation on addition of an electron lends weight to the contention that the formation of the activated complex in the ETC cycle may involve cleavage of the metal-metal bond.

A further exciting demonstration of the utility of ETC reactions in metal cluster chemistry came with the discovery that is was possible to 'tailor make' heteronuclear cluster compounds from their homonuclear counterparts by way of an ETC reaction.[19] The synthetic strategy involves the use of



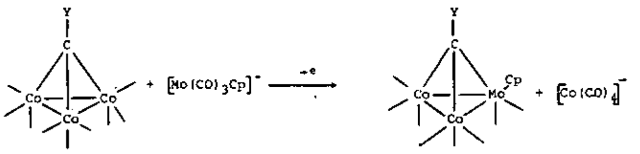
(a)

(b)

Figure 1. Structures of the blue (a) and purple (b) isomeric forms of the complex $(CF_3)_6C_6Co_2(CO)_2[P(OMe)_3]_2$. The trifluoromethyl groups of the 'flyover' ligand and the methyl groups of the phosphites have been omitted for clarity.

a metal carbonyl anion such as $[\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ as the nucleophile in an ETC substitution reaction. Provided the substrate homonuclear cluster can provide a good leaving group (e.g. $[Co(CO)_4]^-$, substitution at the activated complex is followed by extrusion of this leaving group and incorporation of the heterometal atom into the cluster unit,

Equation 5



Against this background, there are a number of ways in which the efficacy of metal clusters as ETC substrates may be further exploited. Exciting possibilities exist in areas where the entering nucleophile is not strongly bound as would be the case with olefins which have recently been shown to act as Lewis bases in cluster ETC processes. One can therefore envisage a dramatic increase in the rate of, for example, olefin isomerisation in the context of an ETC reaction. Other potential nucleophiles such as hydride or enolate anions raise the question of whether the most likely site of nucleophilic attack will be at the metal centre or a carbonyl group of the activated complex. The coordination of reactive intermediates such as the formyl — CHO — group is an intriguing prospect.

ACKNOWLEDGEMENTS. The work described in this article would not have been possible without the skill and dedication of the co-workers mentioned in the references that follow. The structures of many of the fascinating products of ETC reactions were determined with the invaluable assistance of Dr Ward Robinson and his colleagues at the University of Canterbury. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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ORGANOMETALLIC CHEMISTRY AT WAIKATO: A MEANDER AMONG GERMANIUM POLYMETAL CLUSTERS

Ken Mackay and Brian Nicholson
Chemistry Dept, University of Waikato

Ken Mackay graduated from Aberdeen and completed his Ph.D. in Cambridge in 1960, working under Prof. H.J. Emeleus. 1960-70 was spent as Assistant Lecturer, then Lecturer in the Inorganic Chemistry department at Nottingham (Prof. C.C. Addison). He joined the University of Waikato as one of the founder members of the School of Science in 1970 and was appointed Professor and Head of Chemistry in 1979. His research interests cover polygermanium hydrides, germanium-metal species including clusters, applications of molecular spectroscopy, plus occasional ventures into archaeological chemistry.

Brian Nicholson completed his Ph.D. in 1973 at the University of Otago, where he worked with Jim Simpson on metal carbonyl chemistry. After a 2 year post-doctoral position with Professor Mike Lappert at the University of Sussex, working on the ESR characteristics of paramagnetic organometallics, he joined the University of Waikato in 1975. His current research is in organometallic chemistry, especially in the metal carbonyl cluster area, with an associated interest in X-ray crystallography.

In the early years of inorganic research at Waikato, our major interest was in simple systems containing GeMn, GeCo, or Ge_2Fe, with carbonyl ligands on the metal and Ge-H or Ge-CH_3 bonds. Two synthetic routes were commonly employed. The halide elimination reaction of the type shown in equation (1), and the hydrogen elimination of equation (2).

$CH_3GeH_2Br + Co(CO)_4^- \rightarrow CH_3GeH_2Co(CO)_4$ ... (1)

$2(CH_3)_3GeH + Co_2(CO)_8 \rightarrow 2(CH_3)_3GeCo(CO)_4 + H_2$ ... (2)

Simple metal clusters could also be isolated from these reaction mixtures, however, with compounds such as $MeGeCo_3(CO)_{11}$ (Figure 1) and $(Me_2Ge)_2Fe_2(CO)_7$ (Figure 2) being amongst the first to be identified. These compounds were closely related to well-characterised species and could be completely identified by comparison of spectroscopic properties.

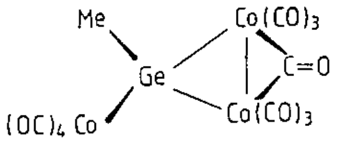


Figure 1

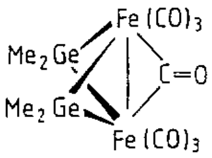
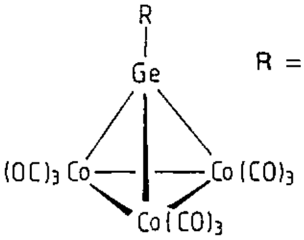


Figure 2

In subsequent work the range of products was extended to polygermane species such as $(H_3Ge)_2GeHMn(CO)_5$, and further polycobalt derivatives such as $(CO)_4CoGeCo_3(CO)_9$ (Figure 3), and $Ge[Co_2(CO)_7]_2$ (Figure 4a).



R = $Co(CO)_4$, Me, Br

Figure 3

Eventually we found we could prepare any of the series $GeCo_4(CO)_n$ for n = 16, 14, 13, and $MeGeCo_3(CO)_n$ for n = 12, 11, and 9. Either of the two synthetic routes, (1) or (2), could be used, though with different products often being obtained in each case. This was found to be a temperature effect and we were able to demonstrate the interconversion $n = 16 \xrightarrow{20°} n = 14 \xrightarrow{50°} n = 13$ for $GeCo_4(CO)_n$, with a similar series for $MeGeCo_9(CO)_n$.

This clarification of the $RGeCo_3$ and $GeCo_4$ systems was immediately offset by the isolation of a number of new, more complex, compounds from the halide system. With the establishment, from these mixtures, of $[GeCo_5(CO)_{16}]^-$, $[Ge_2Co_7(CO)_{20}]^-$ and $[Ge_2Co_7(CO)_{21}]^-$ disappeared the feeling that we could predict products in the system! An early wrestle was with a species which unexpectedly contained mercury, $[GeCo_5Hg(CO)_{17}]^-$, which arises in the system where sodium amalgam is used to produce $Co(CO)_4^-$.

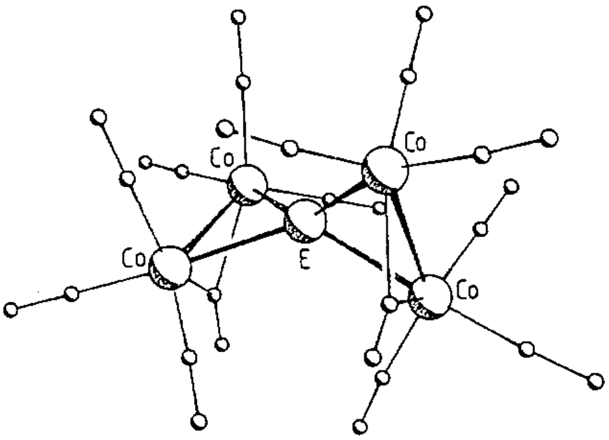


Figure 4a, E = Ge, 4b, E = Si

The most interesting anion is $[GeCo_5(CO)_{16}]^-$, which has a unique 5-coordinate germanium (Figure 5), with the now-familiar $GeCo_2$ and $GeCo_3$ units sharing a common building block. This was shown to form by addition of $Co(CO)_4^-$ to $Ge[Co_2(CO)_7]_2$.

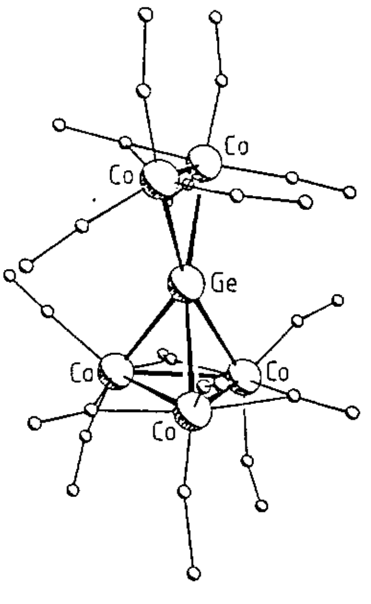


Figure 5

Attempts to prepare a mixed metal cluster using $Mn(CO)_5^-$ in the same reaction lead to $(CO)_5MnGeCo_3(CO)_9$, which could also be prepared by addition of the metal substituted germane to $Co_2(CO)_8$, equation (3).

$$H_3GeMn(CO)_5 + \tfrac{3}{2}Co_2(CO)_8 \longrightarrow (CO)_5MnGeCo_3(CO)_9 + \tfrac{3}{2}H_2 + 3CO \ldots (3)$$

In the last few years, this field has further ramified. Our first silicon species, $Si[Co_2(CO)_7]_2$, figure 4b, was prepared. Also Ge-Ge bonded substrates were used to see if polymetallic species retaining Ge-Ge could be produced; for example Ge_2H_6 might form $(CO)_9Co_3Ge\text{-}GeCo_3(CO)_9$ which could be viewed as a pseudo-acetylene. Instead reactions like (4) were followed, where no Ge-Ge bonds are retained in

$$Ge_2H_6 + Co_2(CO)_8 \longrightarrow Ge[Co_2(CO)_7]_2 + Ge_2Co_6(CO)_{20} \ldots (4)$$

the products. Reagents with the stronger Ge-Si bond still gave only cleavage products, but provided a cleaner route to the Ge_2Co_6 species (5).

$$Me_2Si(GeH_3)_2 + Co_2(CO)_8 \longrightarrow Ge_2Co_6(CO)_{20} \text{ (+ } Me_2Si\text{-}Co \text{ and } Me_2Si\text{-}O \text{ species)} \ldots (5)$$

Addition of germanes to preformed clusters also built up species with separated Ge atoms, as in equation (6).

$$Me_2GeH_2 + GeCo_4(CO)_{14} \longrightarrow \{(\mu\text{-}Me_2Ge)Co_2(CO)_6\}Ge\{Co_2(CO)_7\} \ldots (6)$$

Ge_3H_8 gives what is probably an even higher molecular weight cluster, (7).

$$Ge_3H_8 + Co_2(CO)_8 \longrightarrow Ge[Co_2(CO)_7]_2 + Ge_2Co_6(CO)_{20} + Ge_3Co_8(CO)_{26} \ldots (7)$$

A quite new turn resulted when $MeGeH_3$ was used in place of Me_2GeH_2 in (6). All these reactions involve sealing the components with solvent in a glass tube and leaving them in the dark at room temperature. Reaction times vary from a few hours to many days. It happened that the methylgermane reaction was not opened until after 6 months and it yielded $Me_2Ge_2Co_4(CO)_{11}$. This showed an unusual infrared spectrum and a mass spectrum indicating $2CH_3$ groups (which we kept trying to force into a CO!). Good crystal data were obtained and showed the pseudo-octahedral structure of Figure 6a. Here was a second type of 5-coordination for Ge and an entirely new structure for Group IV — transition metal clusters, although similar species involving P, S, Co and Fe are known. A shorter reaction time allowed us to isolate the expected intermediate. $\{(\mu\text{-}CH_3GeH)Co_2(CO)_6\}Ge\{Co_2(CO)_7\}$ and to demonstrate its rearrangement on standing or gentle heating. Finally, this circle was closed by observing the gentle decarbonylation (8).

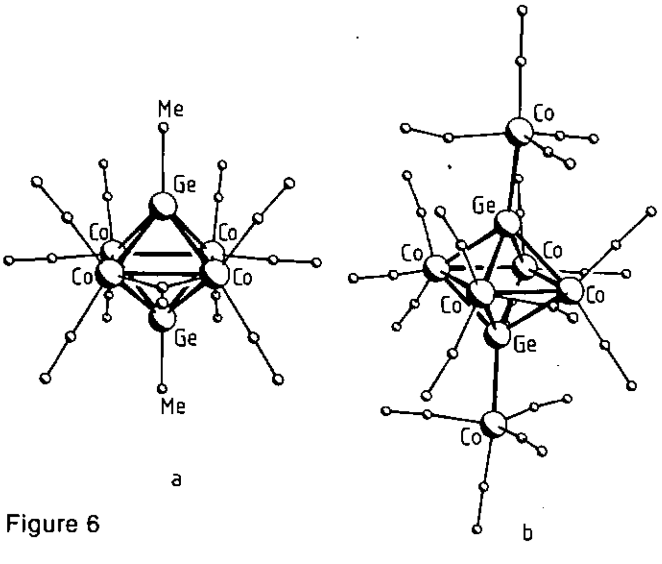


Figure 6

$$Ge_2Co_6(CO)_{20} \xrightarrow{50°C} Ge_2Co_6(CO)_{19} + CO \ldots (8)$$

where the product has the same pseudo-octahedral Ge_2Co_4 structure with terminal $(CO)_4Co\text{-}Ge$ groups (Figure 6b).

PRESENT AND FUTURE

If $Ge_3Co_8(CO)_{26}$ is indeed a product of (7), then by analogy with (8) it too may undergo condensation — to a cubic Ge_3Co_5 unit possibly.

Ge-H bonds readily form Ge-Co, even when Ge is bonded to metals. We are looking at $Ge_2H_5Mn(CO)_5$ with $Co_2(CO)_8$ [compare (3)], and there is a whole host of further possibilities here: consider $(H_3Ge)_2Fe(CO)_4$ or $[GeH_2Fe(CO)_4]_2$.

Anion attack is an equally fruitful field, less predictable but with an exciting range of products. Thus the reaction of $Co(CO)_4^-$ with $Si[Co_2(CO)_7]_2$ gives $[SiCo_9(CO)_{21}]^{2-}$, the first encapsulated Si species and one of the few paramagnetic clusters (Figure 7).

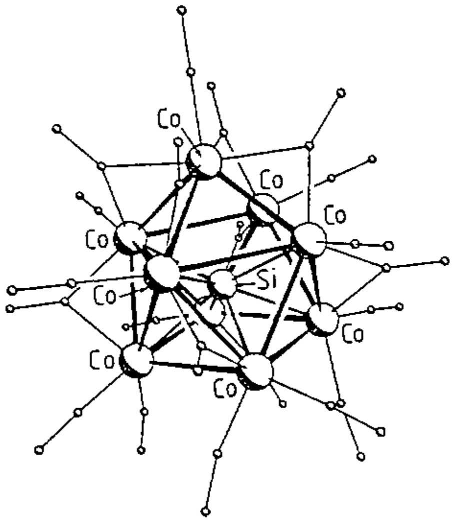


Figure 7

The synthetic field for open and closed clusters stretches indefinitely and we hope to continue its exploration with a grant from the Petroleum Research Fund, administered by the American Chemical Society.

So far, we have done little chemistry with these compounds but, with a relatively unreactive Group IV element to hold the metal atoms together, these species have potential as homogenous catalysts. We are pleased that Tony Sims has gained an NZERDC studentship to explore possible applications.

This article is a sketch of some of the work described in the University of Waikato D. Phil. theses of Bruce Graham (1973), Alan Bonny (1976), Rob Gerlach (1978), Fook Sin Wong (1978), Neil Duffy (1980), Judy Christie (1981) and Steve Foster (1982); and in the M.Sc. theses of Ralph Thomson (1981), Cham Chee Ngo (1981) and Tony Sims (1984).

For a fuller description of the work in this area see: K.M. Mackay and B.K. Nicholson, Chaper 43 of *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982; K.M. Mackay, B.K. Nicholson, W.T. Robinson and A.W. Sims, *J. Chem. Soc., Chem. Commun.*, 1984, 1276; S.P. Foster, K.M. Mackay and B.K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1982, 1156 and references therein.

We are grateful to Ward Robinson, Christchurch, and Tony Jones, Auckland for providing X-ray data for the structural studies. Progress in this area would be considerably slower without ready access to crystallographic facilities. We also thank the U.G.C. for facilities and for scholarships to most of the students listed above.

COUNCIL NEWS

The Standing Committee — Mr Mackney, Drs Denny and Rogers — met in Auckland on 6th November to conduct business on behalf of Council which meets next in Wellington 7/8 February 1985.

The Royal Australian Chemical Institute has advised that it has elected Mr Mackney an Honorary Fellow during his term of office as President of NZIC.

1984 Easterfield Award. From the five entries, which were of a high standard, Dr T. Brittain, Lecturer in Biochemistry at the University of Auckland, was awarded the 1984 Easterfield Medal. This will be presented to him at the NZIC/NZBS Conference in Christchurch in August 1985.

Overseas Visitors. Standing Committee received an appreciative report from Dr Cecil Johnson, Applied Biochemistry Division, DSIR, on the visit of Dr Anne Dell, 6-11 September, to Wellington, Palmerston North, Hamilton and Auckland. In her lectures — "Applications of Fast Atom Bombardment Mass Spectrometry to the Analysis of High Molecular Weight Biopolymers" — Dr Dell emphasised analytical problems in Biochemistry based on her experience as a lecturer in the Department of Biochemistry at Imperial College, London.

Dr A.J. McQuillan, Chemistry Department, University of Otago, is arranging a visit by Professor R.E. Hester possibly in March 1985.

Annual Conferences 1986, 1987, 1988. Dr Rogers reported that Otago Branch had agreed to host the NZIC/NZBS Conference in 1986, Auckland the 1987 one and in 1988 Manawatu. This arrangement interchanges the usual sequence of Otago and Manawatu meetings.

Membership Committee. On the recommendation of the Auckland Branch, Mr R.H. Hopgood, FNZIC, Development Manager, Chemiplas Agencies Ltd, was appointed a member of the Membership Committee for three years from 1st January 1985. He will replace Dr A.F. Wilson, FNZIC, General Manager Kinleith Industries, whose three year appointment ends 31/12/84. Dr Wilson has indicated he does not wish to continue as a member of the Committee. Council expresses its appreciation of his service.

Non Corporate Grades of Membership. Standing Committee advises members that the Auckland Branch is the only one to favour revising the rules from the status quo with respect to the grades of non corporate membership.

Auckland, which has 55% of the 20 Technician and 56 Associate Members, preferred option 2. The only change in this alternative was to combine the Technician (NZCS) and Graduate (B.Sc.) grades for Student Members to enter on obtaining their academic qualifications.

There was some support for this alternative in the other five Branches but not a majority as reported to the President and General Secretary.

Membership. The following applications and changes of status were approved and resignations accepted. The death of Dr James Melville, President in 1950, was noted with regret.

Honorary Fellowship:
Prof. A.L. Beckwith, President RACI, during his term of office.

Fellowship:
BILLCLIFF, John Shaw BSc(Hons Otago) Otago Boys' High School, Dunedin (HOD Science)
FENBY, David Vernon BSc(Hons Otago) Ph.D (UCLA) Chemistry Dept Otago University, Dunedin (Ass. Professor)
PEAKE, Barrie Michael, BSc(Hons) PhD(Cantuar) Chemistry Dept., University of Otago. (Snr Lecturer)
SMITH, Robin Andrew James BSc(Hons) PhD Otago Chemistry Dept., Otago University, Dunedin (Snr Lecturer)
TEMPLE, Wayne Anthony BSc(Hons) PhD Otago, National Poisons Information Centre, Medical School, Dunedin (Scientific Director)

Membership:
BUCKLETON, John Simon MSc(Auck) Chemistry Divn. DSIR., Auckland (Scientist)
FREEMAN, Roy John BSc NZ Concrete Research Assn. Wellington. (Chemist)
MEINHOLD, Richard Horton MSc PhD(Auck). Chemistry Divn. DSIR, Gracefield. (Scientist)
MORGAN, Keith Raymond BSc(Hons) PhD(Well). Chemistry Divn. DSIR. Gracefield. (Scientist)
MORRIS, Peter John, MSc(Massey). NZ Pharmaceuticals Ltd., Palmerston North. (Chemist)
REABURN, Mrs Wendy Marguerite, BSc. ICI Tasman Ltd., Upper Hutt. (Chief Chemist)
READ, Allan John, MSc. PhD(Cantuar). Chemistry Divn. DSIR, Gracefield. (Scientist)

Associate Membership:
BOOTH, John Herbert NZCS Cadbury Schweppes Hudson Ltd, Dunedin (Industrial Chemist)
JOHNSON, Alan Leslie, NZCS. Quality Control Chemist. Wellcome New Zealand Ltd, Auckland.
MERCER, Colin Edward NZCS. Ivon Watkins-Dow Ltd., New Plymouth. (Environmental Health Specialist)
PARSONS, Brett Winston NZCS NZ Electricity Dept, Hamilton. (Chief Laboratory Technician)

Graduate Membership:
DALE, Mark Patrick BE(Ceramics, NSW) Ceramco Ltd, Auckland (Seconded, Chem Div. DSIR Gracefield)
GARTHWAITE, Harold Robert, BSc. Southland Co-op Phosphate Co., Invercargill. (Lab. Technician)
GILLION, Rachel Barbara, BSc(Hons)(Massey). Science Dept., Waikato Technical Institute. (Tutor in Biochemistry)
GRANT, Murray Charles, BSc. Chemistry Dept., University of Waikato. (MSc Student)
HALLIWELL, Robert John BSc(Tech)(Waikato), 148 Upper Harbour Drive, Auckland
LOVE, Philip MacGregor BSc(Hons)(Otago) McLeod Bros. Ltd., Dunedin. (Chemist)
MAGUIRE, Sean Michael BSc Chemistry Dept., Victoria University, Wellington. (Student)
OXENHAM, Julie Magaret BSc. Chemistry Dept University of Waikato, Hamilton (Student)
*SAMUEL, Clifford BSc(Hons)(Otago). Donaghys Industries Ltd., Dunedin. (Technical Officer)
SIVA, Umapalhy MSc(Madras) Chemistry Dept., Otago University, Dunedin (PhD Student)
THOMAS, Noel Roger BSc(Hons)(Cantuar) Chemistry Dept., University of Auckland (PhD Student)
*WONG, Garduen, BSc(Hons)(Otago). Dental School, University of Otago. (Student

* From Student Member

Technician Membership:
CRUMP, Michael Edward NZCS. Southland Catchment Board, Invercargill. (Charge Technician)
McKENZIE, Graeme James NZCS. Southland Catchment Board, Invercargill. (Snr. Technician)
KENNY, Mrs Frances Mary, NCEA(Ireland). NZ Aluminium Smelters Ltd., Invercargill (Chemical Technician)

Life Membership:
F.D. Dorofaeff, Waikato,
G.W. Vivian, Manawatu,
D.A. Forss, Otago.

Resignations:
G.J. Dougherty — Wellington
B.W. Gilliand — Manawatu
S. Jackson — Wellington
D.G. Payne — Auckland

Overseas Contacts — North America.
Dr D.E. Wright, President in 1982/83, left for North America on MAF business on 3rd November. During his visit Dr Wright has been invited by the American Chemical Society to be its guest and to speak to its members and officers in Washington D.C., New York, Peoria, Salt Lake City, St Louis and Sacramento.

This is a reciprocal visit to those of ACS Presidents, Professors Parry and Basolo, in 1982 and 1983 to NZIC Branches.

Dr Wright is also to visit the Canadian Institute of Chemistry in Ottawa and will take part in PAC CHEM '84 in Honolulu in December. Council has asked Dr Wright to discuss continuing ACS-NZIC collaboration.

Australia. The Honorary General Secretary accepted an invitation from the Chairman and Executive of Australia's CSIRO to attend on 1st November the naming of the Ian Wark Laboratories by the Minister for Science and Technology, the Hon. Barry O. Jones, M.P. Adjacent to Monash University in Melbourne, the new Laboratories will house the Divisions of Chemical and Wood Technology and Applied Organic Chemistry.

Sir Ian Wark, CMG, CBE, FAA, FTS, joined CSIR in 1939 to become the first Chief of the Division of Industrial Chemistry. Under his leadership the Division grew into a group of Divisions, corporately known as The Chemical Research Laboratories. Sir Ian was Director, CRL, before being appointed to the CSIRO Executive in 1960.

He is well known for his work, beginning in 1965, as Chairman of the Commonwealth Advisory Committee on Advanced Education and since 1971 he has acted as Honorary Consultant to CSIRO Mineral Research Laboratories. To mark the occasion Dr Rogers presented a NZIC tie to Sir Ian Wark. Dr S.R. Johns, Honorary General Secretary of the RACI, also attended the ceremony.

While in Melbourne Dr Rogers called on Peter Woodhouse, Executive Secretary of the RACI, at Science House. The RACI is interested in arranging a 1988 joint NZIC/RACI Conference either in Brisbane in August (with post Conference tours to Surfers and the Reef etc) or Hobart in February to mark Australia's bi-centennial. Suggestions are invited for a theme for such a meeting.

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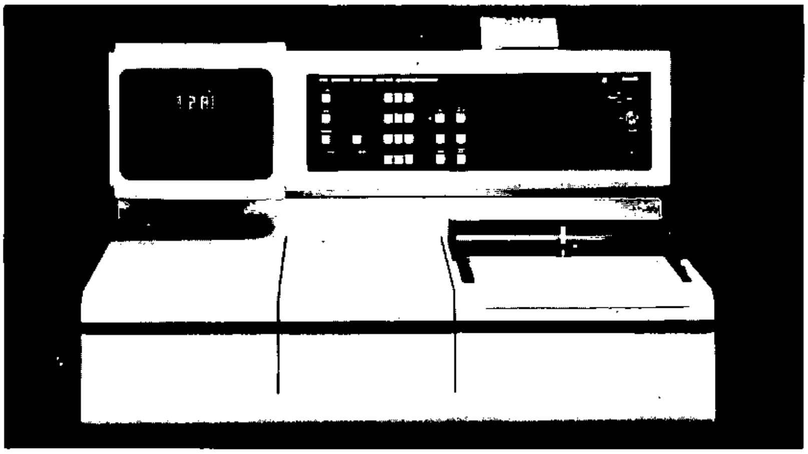

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NOTICES

UNIVERSITY OF OTAGO — DEPARTMENT OF PHARMACOLOGY — POSTGRADUATE DEGREE IN TOXICOLOGY

From the start of the 1985 academic year a post-graduate course in toxicology leading to a MSc degree is being offered within the Department of Pharmacology. The course consists of four papers, usually taken in the first year, with a thesis completed in the second year.

The Department of Pharmacology has associated with it, the N.Z. National Poisons Information Centre, N.Z. National Hazardous Chemicals Information Centre, N.Z. Centre for Adverse Drug Reaction Reporting and the M.R.C. Toxicology Research Unit. Opportunities exist for collaborative studies within the department and throughout the University.

The course is open to graduates preferably with a background in the biological sciences and/or analytical chemistry. Entry is strictly limited.

Enquiries in the first instance should be directed to Professor R. Laverty, Department of Pharmacology, University of Otago Medical School, P.O. Box 913, Dunedin.

The Expert Witness

At the request of the Auckland Branch of the NZIC, the Centre for Continuing Education of the University of Auckland is planning a Seminar on this topic to be held in May of next year. In addition to the NZIC, the seminar is being supported by the Forensic Society, the Medicolegal Society, the Law Society, the Criminal Bar Association, the Police Department, and the DSIR.

A committee has been set up comprising representatives of these various organizations, with Stan Brooker (University of Auckland) as Chairman. Its main task will be organizing the programme and speakers, and we already have agreement from Professor Stuart Kind, at present visiting Professor of Forensic Science at the University of Strathclyde, Glasgow. He was involved in the formation of the Forensic Society of Great Britain, and has served as President and Editor, and has been on Council for 24 years. He is currently writing a book on the science of crime investigation for the Home Office, and recently served on the Commission investigating Police procedures in the "Yorkshire Ripper" case. He will be supported by a distinguished panel of local speakers drawn from the various professions involved.

Further information is available from the Centre for Continuing Education, or from Dr Barry Axon, Chemistry Division, DSIR, Box 2224, Auckland.

NZ Journal of Technology

At the end of this year the NZ Journal of Science will cease publication and be replaced by the NZ Journal of Technology. This new publication is intended to provide a forum for research on a wide variety of applied science and technology subjects. It is hoped that papers will particularly relate to innovation and development relevant to New Zealand industries — small scale/high value technology, as well as large scale/capital and energy intensive.

A special concession subscription rate of $18 p.a. (+ $2 postage) is available to members of the NZIC. To qualify payment must be made through the Institute. Persons wishing to avail themselves of this offer should contact the Registrar as soon as possible.

UNIVERSITY NEWS

Auckland

The seventh IUPAC conference on Physical Organic Chemistry was held at the University of Auckland in the week 20-24 August. Organization was in the hands of a committee of local academics headed by **Peter de la Mare** (chairman) and **Brian Davis** (secretary), and sponsorship from the Royal Society of New Zealand and the NZIC, as well as from IUPAC, was enjoyed. A total of over 200 delegates and spouses from 21 countries attended. Plenary lectures were delivered by **Sir George Porter** (UK), **Peter de la Mare** (Auckland), **Michael Hanack** (West Germany), **Leo Radom** (Australia), **Charles Stirling** (Wales), **Kunio Okamoto** (Japan), **Keith Ingold** (Canada), and **Joseph Bunnett** and **John Bauman** (USA). In spite of conflict with the Wellington NZIC conference, some 25 New Zealand delegates were present. A wide variety of contributed papers and posters on topics related to organic mechanisms and intermediates were presented.

Prof. John Aggett is on leave at Arizona State University, where he will be working with Dr Busack. He will be there until May, 1985.

Massey University

In the second week of October the Food Technology Department held The National Symposium on Food Irradiation, which focussed attention on the potential applications of food irradiation. This process is gaining worldwide acceptance, but is not yet permitted in New Zealand. The process, which involves subjecting food to a mild dose of gamma rays, can be used to disinfest a variety of products providing exporters with an alternative to chemical disinfestation. Irradiation can also increase the shelf life of a range of products. Two eminent world authorities spoke at the symposium, **Dr Hendrik van der Linde,** Head of the Radiation Technology Division of the Nuclear Development Corporation of South Africa (Pty) Ltd and Dr Martin Welt of Radiation Technology Inc., USA. The symposium, wich was organised by **Dr Gordon Robertson,** enabled those involved in New Zealand's food industry to become aware of developments and to discuss the potential applications of food irradiation for New Zealand.

Victoria

Professor R.J. Ferrier presented a plenary paper at the IUPAC Synthesis Meeting in Freiburg (F.R.G.) and visited several German Universities before moving to Heriot-Watt University (Edinburgh) where he will remain on leave until December.

Canterbury

Members of the Chemistry Department were saddened by the untimely death of **Christine Ramsay,** an M.Sc. student, in a climbing accident on October 28. Her cheerful personality will be missed.

Dr R.G. Searle, University of Adelaide, is spending leave in the Chemistry Department, September-December. His research interests are in the area of inorganic coordination chemistry.

Dr D. House has been awarded a Claude-McCarthy Fellowship to spend leave in Basel, Switzerland, with **Professor S. Fallab,** November '84 - June '85. He will also be attending the Royal Institute of Chemistry Inorganic Mechanisms Group Meeting in London, December 18-19.

Dr D.A.R. Happer will be on leave at the University of Sussex for 12 months from November '84, working with **Professor C. Eaborn.**

Dr M.G.H. Munro will visit the Harbor Branch Foundation and universities in the United States and will also attend the PAC Chem '84 Congress in Honolulu while on leave 12 November-22 December.

Dr C. Freeman attended the 12th AINSE Conference on Radiation Chemistry at Lucas Heights, Australia, in November.

Professor L. Phillips has been awarded a Fellowship from the Japan Society for the Promotion of Science to visit the University of Tokyo and the Institute for Molecular Sciences, Okazaki, December '84-February '85. He will also attend the PAC Chem '84 Congress in Honolulu.

Otago

From the Pharmacy Department, **Dr R.H. McKeown** and **Wong Ooi** attended the IUPAC Conference on Physical Organic Chemistry held in Auckland in August to present research results. **Dr T. Hung** had a paper presented in his absence at the 1984 HPLC Symposium held in New York. **Dr Hung, Prof. D.G. Perrier** and **Mr D.H. Robinson** have received grants from the Research Committee of the UGC and the Golden Kiwi Scientific Committee for HLPC facilities. Prof. Perrier and Dr Hung also received $45,000 from the MRC for research on microspheres and drug targetting.

Several people visited the Chemistry Department after attending the IUPAC Conference in Auckland. These included (i) **Prof J.F. Bunnett** from the University of California at Santa Cruz who lectured on Reaction Mechanisms Involving Electron Transfer Stages, (ii) **Dr L. Williams** from the University of Durham who spoke on O – and S – Nitrosation, and (iii) **Dr D.G. Morris** from the University of Glasgow who abandoned his intended lecture topic, and spoke instead on Reactivity and Synthesis with Bridgehead Substituted Camphor Derivatives. In October, **Dr Ward T. Robinson** from the University of Canterbury visited and lectured on Aspects of Molecular Structural Analysis. Earlier, **Drs K. Gawne** and **S. Adejolu** visited from Deakin University, Geelong.

From the Chemistry Department, **Drs B.H. Robinson** and **R.A.J. Smith** will be presenting papers at the Pacific Basin Conference to be held in Hawaii, and **Dr K. Hunter** will attend the Annual Meeting of the Sea-air Exchange Programme (SEAREX) to be held at the School of Oceanography, Univesity of Rhode Island, USA. Dr Hunter has also obtained a grant of $78,000 from the NZERDC to continue trace metal studies in the Manuherikia River in Otago.

Misses S.F. Tsai and **A. Downard** submitted theses recently for their Ph.D. degrees. This will bring to eight the number of Ph.D.'s completed in the Chemistry Department this year, together with three M.Sc.'s. Alison Downard will proceed to postdoctoral studies at the University of Southampton.

BRANCH NEWS

Auckland

During October the annual Chairman's Dinner was held at Romford's, and an excellent meal in very pleasant surroundings was enjoyed by all who attended. **Dr Bill Denny** addressed the gathering and spoke about his recent visit to Poland.

Manawatu

At the branch AGM held in October at the Manawatu Polytechnic, the Chairman's Address was given by **Dr Ken Whittle** on "Technician Training in New Zealand". Dr Whittle discussed the development of polytechnics in New Zealand since 1946 and the many varied courses presented by these institutes. He then described the development of the Manawatu Polytechnic and aspects of the prescription for the syllabus of the New Zealand Certificate of Science. After the lecture the audience was given a conducted tour of the Polytechnic's facilities at the Grey Street Campus (Science and Nursing Departments) and saw Dr Alan Furness's Stage 2 chemistry class in action.

Wellington

During September the Wellington Branch visited two sections of the Building Research Association of New Zealand. This laboratory is situated on Moonshine Road near Judgeford.

BRANZ exists to promote building standards, and its services are specifically directed towards the building industry. The Wellington Branch visited the Fire Research Division, which investigates the performance of building materials exposed to fires. One of their aims is to help manufacturers develop products which comply with fire bylaws.

The second section visited was Materials Division which examines the effects of the environment on building materials. This work includes the effects of corrosion, changes in properties of non-metallic materials, and the performance of surface coatings.

The October Meeting was the Branch AGM and Mellor lecture. This year's Mellor Lecture was delivered by **Dr H.K.J. Powell** from Canterbury University. Kip Powell discussed the problems of converting the Pakihi soils on the West Coast of the South Island to useful agricultural production. These soils are formed under acidic litter and subject to high rainfall. The drainage is poor due to the underlying iron pans. These soils require high levels of added nutrients, which are rapidly leached by the rainfall. Kip discussed the nutrients required for pasture production, and the trials to retain the nutrient levels in the pasture.

Canterbury

The September meeting of the Canterbury Branch was addressed by **Dr David Bibby**, Chemistry Division DSIR (Gracefield). At a well attended talk, he discussed the research work being carried out by DSIR staff on the zeolite catalysts to be used in the production of synthetic petrol at Motonui and some of the problems which might be encountered when production commences.

In November, the branch adjourned to St Helenas Wine Estate at Coutts Island where quality white wines are now being produced. After an introductory glass, winemaker **Danny Schuster** talked about the science of oenology, then proprietor **Robin Mundy** introduced members to a range of the Estates wines in a wine tasting session accompanied by excellent food.

Otago

Dr **C.J. Easton**, from the University of Canterbury, addressed the Branch at its meeting in September. He talked about the Battle of Penicillins against Bacteria. The branch AGM was held in October, and on completion of the formal business, **Dr Joan McKenzie** gave the Chairman's Address which she entitled "Group IIB: A Status Report".

Prof. A.D. Campbell (Head of the Chemistry Department) has agreed to chair an organising committee for the Annual Conference of the Institute to be held in Dunedin in 1986. The Otago Schools' Science Fair was held in August. **Richard Tapper** (chemistry teacher) reports that the first prize went to **Mark Milner** of Bayfield High School, Dunedin. Mark's exhibit was a chemical one in which he measured the amounts of kinetic and sound energy released when mixtures of hydrogen and oxygen, and of various hydrocarbon gases and oxygen were exploded in small plastic containers. Mark, representing Otago, also gained first prize at the National Science Fair held in Hastings in September. Other successful chemical exhibits at the Otago Fair included investigations of alcohol in home brew by **Fraser McKenzie**, the production of a paper from grass clippings by **Gretel Darby**, and a study of fibre dyeing by **Juliet Pope**.

GOVT DEPTS & RESEARCH INSTITUTES

Gracefield

The DSIR has appointed **M/s Monica Hissink** as Head Librarian for the Gracefield Campus and DSIR Central Library which will be opening early in 1985.

Mr K. Dalzell of the Applied Chemistry Section recently visited Sabah, East Malaysia, to inspect the coating system on a wharf installation.

Dr K.J.D. McKenzie, head of the Solid State Section at Chemistry Division is visiting China and Japan on a Cooperative Science Liaison Visit to discuss ceramics production and chemistry.

Dr D.R. Crump of the Natural Products Section is spending seven weeks in Canada working with **Dr H. Wieser** at the University of Calgary. This visit was financed by the Applied Mammallian Research Institute to investigate the analysis, synthesis and utilization of mammallian pheremones.

Dr L.Y. Foo has been invited by the President of the Nanjing Institute of Forest Products to visit organizations in the Peoples Republic of China where he will be discussing the chemistry of Tannins.

Dr D.S. Perera attended the Australian Ceramic Society Conference in Sydney during August where he presented two papers on Kaolinite/hallogsite clays. He also visited the Department of Ceramics Engineering of the University of NSW, and the NSW Institute of Technology. Dr Perera, **Mike Rose** and **Vaughn White** are continuing with contract research for the ceramics industry in the new solid state chemistry section.

Wairakei

Dr K.L. Brown and **Dr R.B. Glover** are visiting the Phillipines on geothermal studies.

Christchurch

Geoff Mills is to take up a four year appointment at the University of Waikato, Chemistry Dept, commencing 1985.

HEALTH DEPARTMENT

Wellington

Mr J.E. Reeve, presented a paper on 'The Health Departments Priority Programme on Organophosphate Pesticides' at the Ninth International Congress on Agricultural Medicine and Rural Health which was held in Christchurch. Proceedings of this meeting are available from Conference Management Services, PO Box 3030, Wellington (Cost $25.00 + $1.00 pp).

Mr Reeve also attended the 24th meeting of the Australian Environmental Council's National Advisory Committee on Chemicals held in Sydney during October. The main topic of this meeting was the Australian National Notification and Assessment Scheme for Chemicals.

The principal Toxicologist **Mr M. Bates** is visiting the Phillipines for two months to consult on pesticide toxicology.

Mr J. Waters has recently returned from the University of Surrey where he completed an MSc in Toxicology. His thesis topic was 'Proteinurea and Heavy Metal Toxicity in Humans'.

NECAL, Auckland

The National Environmental Chemistry and Acoustics Lab. has had two recent arrivals from the northern hemiphere. **Rosemary Totton** has returned after spending six months in the UK on a technician's Commonwealth Travel Award. **Annemarie Steinmeijer**, a Ph.D. student at the Wageningen Agriculture University, Netherlands, has also arrived to work for three months in the chemistry lab.

DAIRY RESEARCH INSTITUTE:

Dr Steve Haylock recently attended "Milk Proteins '84" in Luxemburg. Subsequently he visited European equipment manufacturers and the Dairy Board subsidiaries, General Milk Products in Hamburg and N.Z. Milk Products in California.

Dr Alastair MacGibbon has joined the Milkfat and Butter Section as a Research Officer to investigate fundamental aspects of the physical chemistry of edible fats.

Derek Knighton has joined the Protein Chemistry Section to investigate the effect of freezing temperatures on milk and to continue studies on conformational changes in milk proteins.

Dr Frank Martley of the Cheese Technology Section recently returned from study leave at the CNRZ Dairy Microbiology Laboratory, Jouy-en-Josas, France, where he investigated aspects in the manufacture of soft ripened cheeses.

Ms Lee Huffman is spending 15 months as a Fulbright Scholar at the DRI. She is working on accelerated ripening of cheese with the Flavour and the Cheese Technology Sections.

(continued on Page 166)

SCHOOL CHEMISTRY COMPETITIONS

The Branches of the Institute appear to be making increasing efforts to develop an interest in chemistry in local schools. A variety of competitions have been organised, usually with the willing support of the universities or government laboratories. The reports below do not cover all of the activities in this field, but serve to illustrate and highlight these efforts.

UNIVERSITY OF AUCKLAND/ NZIC SCHOLAR OF THE YEAR

This competition was held at the University on 15 August. Invitations were sent to all secondary schools in the area to enter up to three 7th Form students each. A total of 46 competitors from 22 schools took part.

The competition took the form of two laboratory exercises and a written test, organised by *Dr Cliff Richard* and *Dr Roger Whiting*. This was followed by a tour of the Chemistry Department, and an entertaining lecture by *Prof. Brian Davis*. The top four contestants from the first section then took part in a chemical "mastermind" quiz hosted by *Dave Wilkins*. Prizes to *Michael Neeve* (1st), *Rowan Grayling* (2nd), *Stephen Mackay* (3rd) and *Micheala Saigh* (4th) were presented by branch chairman, *Bill Denny*.

MANAWATU BRANCH — SCIENCE FAIRS

The Tenth Manawatu Science Fair was held in the Centennial Convention Centre, Palmerston North, during 15-19 June. Institute members who assisted with the Fair included *Drs Ian Watson* (Fair Committee), *Ted Baker* and *David Parry* (Judges), *Ken Whittle* and *Cecil Johnson* (N.Z.I.C. Manawatu Branch Prizes Judges). Exhibits were grouped into four subject classes namely, biological, social, physical and earth sciences, each at three age levels — intermediate, secondary and senior. Winners of the Manawatu Branch Prizes were *C. Humphrey* and *A. Bevan* in the Intermediate Class for their exhibit titled "Plant Power" and *J. Brodie* and *M. Cavanagh* in the Secondary Class for their exhibit titled "Can You Fool Shopkeepers?" Both of these exhibits were concerned with electrochemistry, the first illustrated the production of different voltages with different pairs of metals and the second demonstrated various aspects of electroplating.

In August, two Science Fairs were held on either side of the North Island. The Manawatu Branch provided prizes for exhibits at both of these events. The Third Gisborne Science Fair, held from 8-14 August in the Gisborne Army Hall, attracted 63 entries from three intermediate schools and three high schools. The Branch Prize was won by *Ann Ross, Rachel Rissetto, Sharyn Willan, Mandy Thorp* and *Karen Patterson* from the Gisborne Girls' High School for their entry in the Intermediate biology Section entitled, "Water Pollution in Gisborne". *Mr Murray Ferris*, Kiwanis Club Convenor of the Fair, believes that next year's event will be even better than this year's, with the participation of more schools in the region.

The Second Taranaki Science Fair was held at the New Plymouth Boys' High School during 17-18 August. This Fair attracted 120 exhibits. the Prize winners were *Tina Shilvock* and *Juliana Mansvelt* from Hawera High School with their exhibit entitled, "The Hair Affair". *Dr Chris Kirk* commented that this Science Fair was much better organised than last year's, with a more professional approach being made to the many necessary details, and that the good support given by the many exhibitors and visitors ensured its success for the future.

WELLINGTON — ANALYTICAL CHEMISTRY COMPETITION, 1984

Earlier this year the Wellington Branch invited secondary schools in the Wellington Branch region (including Marlborough, Nelson and the Wairarapa) to the competition, which involved the analysis of a solution containing ferrous ion, for its concentration. Eighteen schools took part.

Most entrants used the method of titration of the sample with potassium permanganate solution after standardising the latter with ferrous ammonium sulphate solution or oxalic acid or similar. About one-third of the 30 individual entries (maximum of 2 per school) provided a result within 1.5% of the reference analysis of 0.0923 moles per litre, ±0.0005 (standard deviation). It was therefore a very close contest and the judges had to decide on the winning entry on the basis of the laboratory reports provided (generally of a high standard) from the top group of 4 entries. The judges also decided to add a commended category to the award list to acknowledge the efforts of a group of entrants close to the top group in terms of results and standard of report.

Winning School: ($50 plus Champion Certificate) St. Mary's College.

Highly Commended: (Certificates) Onslow College, Rongotai College, Samuel Marsden Collegiate School.

Commended: (Certificates) Chilton St. James, Rongotai College, Upper Hutt College, Wainuiomata College, Wellington East Girls College (2).

WAIKATO BRANCH — ANALYTICAL CHEMISTRY COMPETITION

The Waikato Branch inaugurated this year what is hoped to be an annual analytical chemistry competition for senior high schools students. Entrants were required to determine the concentration of samples of aqueous phosphoric acid sent out to them. A total of nineteen entries throughout the Waikato-Bay of Plenty area were received, and the quality of entries was sufficiently high to present the judges with a difficult assignment. Joint winners were *Darrel Malaquin* and *Roger McCabe* (Rangitahi College, Murupara) and *Harvey and Roger Rigby* (Whakatane High School), the $50.00 prize in each case being for the purchase of chemistry texts for the school library. The winning entries were displayed at the Hamilton Science Fair in July.

Busy trying to identify metal cations in aqueous solution are 7th formers Sandra Law, Nga Tawa College (left), Kenneth Bidlake, St. Peter's College (centre), and Nicola Dinley, Nga Tawa College (right).

MASSEY UNIVERSITY COMPETITION

Six hundred 6th and 7th form science students from the Manawatu, Hawkes Bay and Wanganui areas recently converged on Massey University to carry out experiments in the University's chemistry laboratories. The theme this year was "Analytical Chemistry" and was concerned with the identification of some common metal ions in solution using simple chemical reactions. Students also had a chance to use a simple spectrophotometer to determine permanganate concentrations. In addition to the laboratory course which took about 2 hours, *Mr Mark Pritchard*, Senior Analyst in the DSIR's Grasslands Division, gave an entertaining and informative talk on modern analytical chemistry.

Visits to Massey University by school science students are now an annual event. *Dr Andrew Brodie* who organised this year's exercise said, "Over the six years the programme has been running it has proved to be a worthwhile introduction to university chemistry for the students, and also helps the University to maintain contact with the region's science teachers."

1984 NOBEL PRIZE IN CHEMISTRY

The 1984 Nobel Prize in Chemistry has been awarded to a biochemist, Professor Robert B. Merrifield of the Rockefeller University, New York, for his development of the automated chemical synthesis of peptides and proteins. Following work on the conventional fluid-phase peptide synthesis in the mid-1950s, Merrifield first reported his two-phase system in 1962.

The key to the method is the esterification of the initial amino acid (which becomes C-terminal in the completed polypeptide) to a derivitised polystyrene resin. The sequential coupling of each additional amino acid by carbodiimide, (and the "blocking" reactions necessary to protect other reactive groups during coupling) can be carried out rapidly and in high yield because the solid-phase product can readily be separated from the liquid-phase reactants and by-products. The final step in the sequence is the cleavage of the completed polypeptide from the resin. Bradykinin, a hypotensive nonapeptide, was synthesised in 68% overall yield in 1964, and in the following year an automated procedure achieved the same yield in 32 hours. Merrifield reported the first total synthesis of an enzyme (ribonuclease A, consisting of 124 amino acids) in 1969. In that year, it was estimated that 328 other synthetic peptides had been prepared using the solid-phase method. There has been continuous development of the apparatus, the resins and, in particular, of the chemistry of the blocking reactions, by Merrifield and others. Several commercial versions of the apparatus are now available.

Apart from its obvious application to the synthesis of biologically-active peptide hormones and antibiotics normally found in minute quantities, Merrifield's method has been invaluable in confirming tentative peptide structures (by the demonstration of biological activity in synthetic duplicates), and in exploring the relationship between structure and biological activity by the synthesis of modified forms of peptides. In recent years, the method has acquired new significance as an adjunct to recombinant DNA technology. It is now possible to deduce the structure of antigenic proteins present in viruses from the corresponding nucleotide sequences in the viral DNA. Peptides can then be synthesised and used for immunisation, giving rise to vaccines which are safe because they are not derived from any viral product. This technique was used to produce a vaccine against foot-and-mouth virus in 1982 and more recently has been extended to human hepatitis vaccines.

Ken Scott,
Dept of Biochemistry,
University of Auckland.

GOVT' DEPTS

(Continued from Page 164)

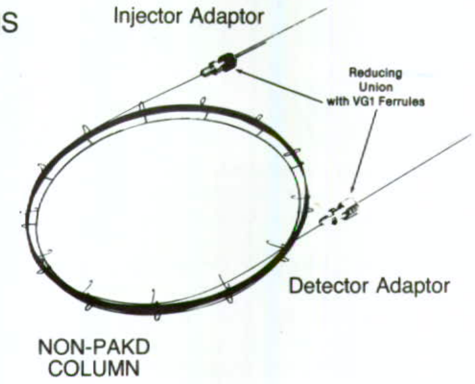
MAF, Invermay

Two people have joined the staff of the Invermay Agricultural Research Centre recently — **Greg Hormann,** who recently graduated M.Sc. at Otago University, and **Dr Alberto Cohen,** a Research Fellow from Holland who will stay for two and a half years funded by the Liquid Fuels Trust Board. Both will be involved with the development of biogas technology. The Soil Section, headed by **Dr Rex Dolby,** launched the Computerised Soil Advisory Service recently. This collates data for pastures and crops, and recommends the level of replacement of nutrient losses incurred.

At the Invermay Animal Health Laboratory, interest in the iodine status of sheep in the southern region has prompted a project involving 13 properties in Central Otago, where the ewe intake of this element, and its transfer to the lamb, is being investigated. While this is primarily concerned with the detection of goitre and with lamb survival, further trials will deal with the general effects of subclinical iodine deficiency on the reproductive performance of selected flocks.

OBITUARY

We note with regret the death earlier this year of **Dr J.C. Smith,** at his home in Somerset, England. A graduate of Auckland University College (M.Sc, 1922), Dr Smith was an 1851 Exhibition Science Research Scholar, and gained a Ph.D from Manchester University in 1925. For most of his career as an organic chemist, Dr Smith was on the staff at Oxford, where he was awarded a D.Sc. in 1941. He retired in 1966 and undertook the writing of a history of Organic Chemistry in Oxford, Part I, the Perkin Era, being published in 1969, and Part II, the Robinson Era, in 1975.



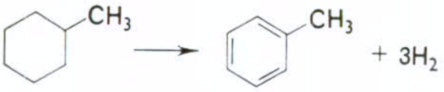
Some Catalyst Applications in New Zealand

A.C. Herd Auckland Technical Institute and
J.E.A. Reece Swift Consolidated NZ Ltd

Because of the importance of catalysts to chemical industry, it would be an impossible task to exhaustively survey all of the catalyst applications in New Zealand. Furthermore, many specific applications are industrial secrets and the companies involved and the catalyst suppliers are understandably unwilling to divulge full information. This article, therefore, considers only some of the many possible examples and has been sourced partially from catalyst manufacturers' literature provided by their New Zealand agents. These agents are listed at the end of the paper and the reader reply card should be used for further information.

Petroleum and Related Products

The original Marsden Point Refinery was built to refine light Iranian crude and condensate from the Kapuni Gas Plant using Shell technology. The catalytic reforming process uses a platinum — rhenium based catalyst which increases the aromatic nature of the product and also its octane number by means of reactions such as the dehydrogenation of naphthenes, dehydrocyclization of paraffins, isomerisation of paraffins and hydrogenation of alkenes. Some desulphurisation also occurs, but Marsden Point has a hydrodesulphurisation process using a cobalt-molybdenum catalyst supplied by Shell in Holland.



In the Marsden Point extensions currently underway, a hydrocracker is being installed so that heavy crudes can also be refined. At this stage the particular catalysts to be used are not widely known as the unit will be supplied as a package deal with specified catalysts to guarantee operation. Usually after the plant has been running successfully for a stated period a tender is let for the supply of catalysts for continued operation.

The process of producing gasoline from natural gas has been described in Chemistry in New Zealand, *43* 199 and *45* 53. The Motonui plant which will come on stream in early 1985 will first desulphurise the natural gas using a zinc oxide catalyst, then reform it to a mixture of carbon monoxide, carbon dioxide and hydrogen over a nickel catalyst. After catalytic conversion to methanol, the Mobil process for the conversion of methanol to gasoline will involve a zeolite catalyst in the hydrogen form, its 0.5 nm pore size giving size selectivity resulting in a product very similar to petrol derived from crude oil.

Methanol is produced from Natural Gas by the ICI process at the Petrolgas plant at Waitara. The natural gas is first desulphurised using a zinc oxide catalyst, reformed then converted to methanol over a copper catalyst.

Ammonia/Urea

The chemistry involved in the plant at Kapuni in Taranki has been described in Chemistry in New Zealand *43* 141. The natural gas is first passed over a bed of zinc oxide pellets to remove any hydrogen sulphide. Steam is then added in the primary reformer where a catalyst contains 15-17% nickel oxide on a magnesium aluminium oxide carrier. The secondary reformer contains a nickel catalyst with 9% nickel oxide and completes the reaction.

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

air is also introduced to provide nitrogen and oxygen.

The shift reaction, can be done in two stages, over an iron based catalyst, and a catalyst with a copper and chrome base. This converts much of the CO to CO_2 and produces additional hydrogen.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The carbon dioxide and remaining carbon monoxide are removed and the resulting gas stream, now essentially nitrogen and hydrogen, converted to ammonia over an iron oxide catalyst. Ammonia and carbon dioxide can then be reacted to give urea.

Town Gas Supply

The town gas supply in New Zealand is now, in the North Island, based almost entirely on Natural Gas, and the gas companies have become reformer gas manufacturers. e.g. in Auckland they use Zimmerman Catalyst Reformers.

In the South Island i.e. the Dunedin City Council use a cyclic reforming plant which uses a light flash distillate as a feedstock. The gas is formed by passing the feedstock, together with steam over a Nickel Catalyst heated to 800 deg C. Eventually Natural Gas will be used in both North and South Islands as a feedstock for the Town Gas Supply industry. In the North Island the Natural Gas will be reticulated by pipeline throughout the Island while in the South feedstock will be transported to Dunedin and Lyttelton by sea-going tankers.

Sulphuric Acid

After burning sulphur to give sulphur dioxide, it is oxidised to sulphur trioxide over vanadium pentoxide with potassium sulphate on a porous silical support. Sulphuric acid is produced by five fertiliser companies in New Zealand, between them operating ten sulphuric acid plants. Nearly all of the plants use the Monsanto process and a Monsanto catalyst.

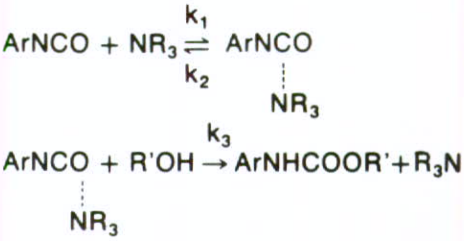
The Polymer Industry

Formaldehyde (Chemistry in New Zealand *46* 92) is manufactured in New Zealand by two companies the reaction.

$$CH_3OH + \tfrac{1}{2}O_2 \longrightarrow CH_2O + H_2O$$

being catalysed by silver catalysts.

Tertiary amines are used as catalysts in polyurethane foam production, accelerating the reactions between isocyanate and organic hydroxyl groups and between isocyanate and water. A complex is formed between the isccyanate and the amine. The complex then reacts more rapidly with the hydroxyl compounds than a free isocyanate molecule.



$$\mathrm{ArNCO + NR_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \begin{matrix}ArNCO\\ \vdots\\ NR_3\end{matrix}}$$

$$\mathrm{\begin{matrix}ArNCO\\ \vdots\\ NR_3\end{matrix} + R'OH \xrightarrow{k_3} ArNHCOOR' + R_3N}$$

With the formation of the urethane linkage, the amine is set free. Complex formation is due to the Lewis base nature of the amine (unshared electron pair) and its interaction with the carbon of the isocyanate with a consequent shift in electronic structure to a more reactive form.

The polyurethane foam reactions can also be catalysed by metal compounds e.g. stannous octoate.

Methyl ethyl ketone peroxide solutions are also marketed in New Zealand for polyester catalysts.

Edible Fats and Oils

Unsaturated triglycerides are hydrogenated with hydrogen over a nickel based catalyst to alter the physical properties of a fat or oil. For example coconut oil which melts at 26°C can be converted to more solid products used in biscuit fillings.

From crude oil cracking to biscuit fillings, catalysts play diverse roles in New Zealand's chemical industry. The following list of companies either import or manufacture catalysts and should be approached for more detailed information.

BASF

Produce a wide range of catalysts for gas production, conversion, purification, syntheses, oxidation, the oil industry and hydrogenation. BASF also produces a ranges of catalysts for sulphuric acid production.

Circle **11** on the reader reply card.

Englehard

Specialists in precious metal chemicals including catalysts, gold, silver and the platinum group. Englehard also produces a supported catalyst for thermal incinerators under the TORVEX trade name.

Circle **12** on the reader reply card.

WR Grace (NZ) Ltd

Grace Davison Chemical Division produce Raney catalysts, nickel, Cr-promoted nickel and Mo-promoted nickel. Davison also supplies nickel aluminium alloys in granular and powder form.

Circle **13** on the reader reply card.

Hardie Trading Ltd

Agents for Dynamit Nobel and the Hall

(Continued overleaf)

CATALYST APPLICATIONS
Continued

Chemical Company their range of metal salts include many such as the metal acetylacetonates and magnesium alcoholates which are used as catalysts. Also agents for Th. Goldschmidt AG who produce metal salt catalysts for polyurethane foams.
Circle **14** on the reader reply card.

A.C. Hatrick (NZ) Ltd
Agents for methyl ethyl ketone peroxide solutions manufactured by Speciality Chemicals Division of RCI.
Circle **15** on the reader reply card.

Hoechst (NZ) Ltd
Hoechst manufactures a range of nickel and cobalt catalysts for hydrogenation, and copper catalysts for dehydrogenation. Noble metal catalysts are also available.
Circle **16** on the reader reply card.

Johnson Matthey Ltd
Specialise in platinum group catalysts with particular expertise in automotive exhaust purification catalysts. Also Honeycat catalytic air pollution control technology.
Circle **17** on the reader reply card.

Neill, Cropper & Co. Ltd
Agents for Cyanamid catalysts for low temperature cure in solvent-based amino cross-linked coatings. Choice of strong acid, weak acid, and metal salt catalysts. Agents for DABCO (triethylene diamine) from Air Products and Chemicals Ltd a polyurethane foam catalyst. Agents for Pricat nickel catalysts from Unichema International for the hydrogenation of oils and fats.
Circle **18** on the reader reply card.

Shell Chemicals NZ Ltd
Catalysts for petroleum refining.
Circle **19** on the reader reply card.

Swift Consolidated (NZ) Ltd
Agents for Nissan Girdler catalysts, the range covers, hydrogen and synthesis gas manufacture, gas purification, hydrotreating of oil fractions, hydrogenation and dehydrogenation catalysts, special catalysts e.g. sulphuric acid production, formaldehyde production.
Circle **20** on the reader reply card.

Union Carbide NZ Ltd
Amines for the polyurethane industry.
Circle **21** on the reader reply card.

ANALYTICAL INSTRUMENTATION IN THE FOOD INDUSTRY

Modern analytical instruments are playing an increasingly important role in food processing. These laboratory instruments provide quick and precise measurements that enable food producers to determine the quality of ingredients and final products, to identify chemicals that could enhance or spoil the products and to analyze the processing and packaging procedures that affect the shelf life of the products. Analytical instrumentation also helps the food industry to comply with federal requirements for quality control procedures.

These instruments fall into four categories — they are used for the identification and quantitification of chemical elements, the separation of substances, the analysis of molecular structures and for automation of the instruments and for collating and reporting results of the procedures.

Spectrophotometers

Food technologists use the UV/visible spectrophotometer to assay products in quality control, including the inspection of color. The primary purpose of this type of inspection is to maintain visual appeal of the product.

UV/visible spectrophotometers are also used to identify and determine the purity of food dyes, to determine the types of sugars in a mixture, the relative quantities of those sugars and the sugar concentration in canning, syrups and other products to maintain the quality and profitability of the process.

Most commonly used in qualitative determinations, infrared spectroscopy is regarded as the most important identification technique in organic chemistry and is the most widely used.

Both UV/visible and infrared spectrophotometers measure fats and oils in processed foods, especially those that are fried and roasted. Measurements are used for the identification of oils, the fat content of the oils and the degree of unsaturation of the oils. The measurements can determine rancidity and spoilage of the products.

Spectrophotometers also test for pesticides, herbicides and other dangerous residues that must be eliminated from food products. They are used before processing and for checking the final product.

High-Performance Liquid Chromatographs

High performance liquid chromatography (HPLC) separates chemical mixtures by passing samples in carrier liquids through stainless steel columns densely packed with small particles. Pumps force the liquid through the column. Components are separated by chemical and physical interactions with the packing materials. The components migrate at different speeds through the column, and a detector measures the quantity of each component in the mixture.

In addition to being used alone or in combination with other analytical instruments such as spectrophotometers in the analysis of fats and oils, sugars and sugar alcohols, pesticides, bacterial and fungal toxins, and food dyes (see page 2), high-performance liquid chromatographs play other important roles in organic analysis of food products. HPLC is an effective techniques for separating and determining organic acid concentration in citrus fruits, fruit juices and wines. The types and quantities of organic acids determine the flavour, aroma and tang of these foods.

HPLC separates, identifies and quantitates vitamins in food and food additives. Food and Drug Administration (FDA) regulations require reporting of vitamin concentration in finished products. Careful control of vitamin content of in-process foods assures consistency with package labelling and manufacturing standards.

Amino Acid Analyzers

Using an advanced form of high-performance liquid chromatography, the amino acid analyzer separates, identifies and measures the free and derivatized amino acids that are the essential components of proteins. By quantifying amino acids with the latest generation analyzers, food technologists can maintain and improve critical qualities in the products.

Amino acid analysis is used to determine the quality of proteins in both natural and processed foods. Ordinary varieties of field corn are low in lysine, an amino acid essential to good nutrition and growth in humans and animals. With the use of amino acid analysis, hybrid varieties of corn have been developed. In the brewing industry amino acid analyzers are used to assure the consistency of flavour in each batch of beer.

pH Meters

Beckman built the first practical pH meter in response to a request from the California citrus industry. Because pH is basic to most natural and artificial processes, the application of pH meters to the quality control of food products involves every facet of food production.

Reliable pH measurements is critical to the proper gelling of jams, jellies and gelatins. It indicates the ripeness of citrus fruit. Keeping tomato products and other canned fruits at a low pH helps to prevent botulism.

In the baking industry pH measurements are used to determine the age of the flour and the proper blends of reducing and non-reducing sugars. Producers of sugar and syrup also use pH measurements to ascertain the proper flavour.

Beverage manufacturers need to determine pH values to increase the shelf life of their products. Examples include lactic acid increase with the age of milk, total acidity in wine and carbonation in beer production.

pH measurements can indicate the degree of degradation of meat products. They also help to monitor the hydroxyl value in oils and fats to detect rancidity in these products.

Ion-selective electrode analysis, an extension of the pH technique, uses electrodes that are designed to be sensitive to the levels of ions other than hydrogen. An example is an ion-specific electrode for sodium, used in determining the sodium content of such products as dietetic canned foods and wine.

Ion-selective electrodes perform concentrated to trace-level analyses of a variety of foods and beverages. Advantages include easy sample preparation and insensitivity to colour or turbidity.

Oxygen Analyzers

Oxygen analyzers measure gaseous or dissolved oxygen in prepared and packaged foods. Oxygen is probably the most common cause of deterioration of packaged foods. By removing oxygen from the headspace of the package and maintaining an oxygen barrier, manufacturers can protect food from changes in original quality, natural flavour and colour. Oxygen analyzers measure the residual oxygen in the headspace of flexible packages, cans and bottles to help prevent oxygen damage, randicity or microbial spoilage.

Oxygen measurements of food products are used in control of food quality during preparation, packaging, storage and shipping. They also are used to study chemical changes, such as oxygen uptake, to improve food production and lessen waste. Dissolved oxygen measurements help to analyze the aging effects and color development of meat; the storage and respiration of fruits; brewing and brewing wastes in beer production; the nutritional value, packaging and quality of milk, the fermentation of yeast and other cultures; the nutritional value and rancidity of edible oils and fats; and the quality control of wine.

Liquid Scintillation Counters

Liquid scintillation counters are highly sensitive instruments used in quantitative analysis. They isolate and measure radioactive substances, especially beta radiation. Samples are taken to the laboratory, and radioactive tracers are added to the samples to aid in the determination of various substances.

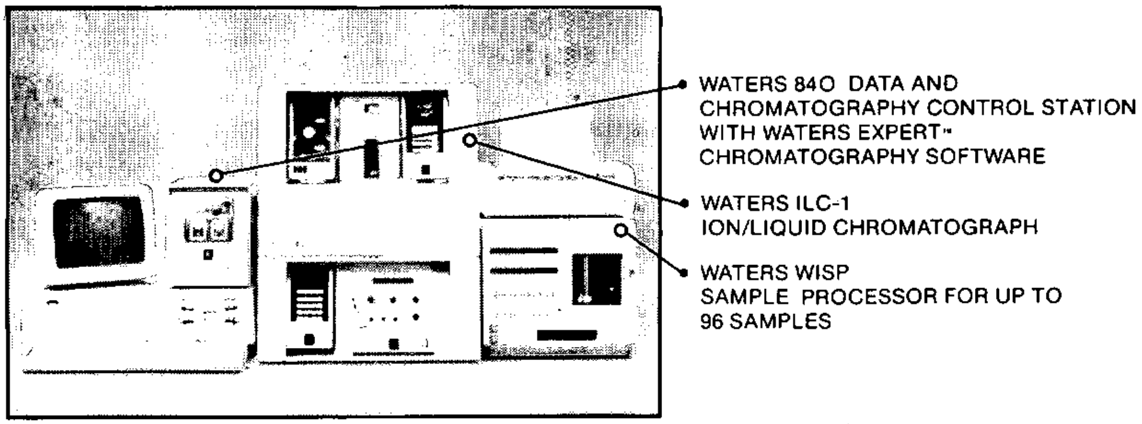
In the food industry liquid scintillation counters are used to determine the amylase content of foods. Amylase, an enzyme, acts as a starch blocker. If the starch content of certain foods such as cheese and puddings is low, the appearance of the food changes. Although low starch content poses no health problems, it affects the shelf life of the food.

Laboratory Automation Systems

Complete customized automated laboratory computer systems from Beckman include hardware, software, interfaces, installation, training, service and consultation. Integrated software and hardware provide automated management of the laboratory, data acquisition, computation, storage, archiving, retrieval, reporting, quality control certification and transmission of data.

The laboratory automation systems are compatible with analytical instruments from any major manufacturer. Thus, they can be interfaced with all analytical instruments used in the food industry and tailored to specific reporting format requirements and laboratory configurations. Specific food industry applications include food stability and shelf life testing, content uniformity analysis and quality control testing.

This article was prepared by Beckman Instruments Inc. for further information, contact their NZ agents, Alphatech Systems Ltd, or circle 22 on the reader reply card.



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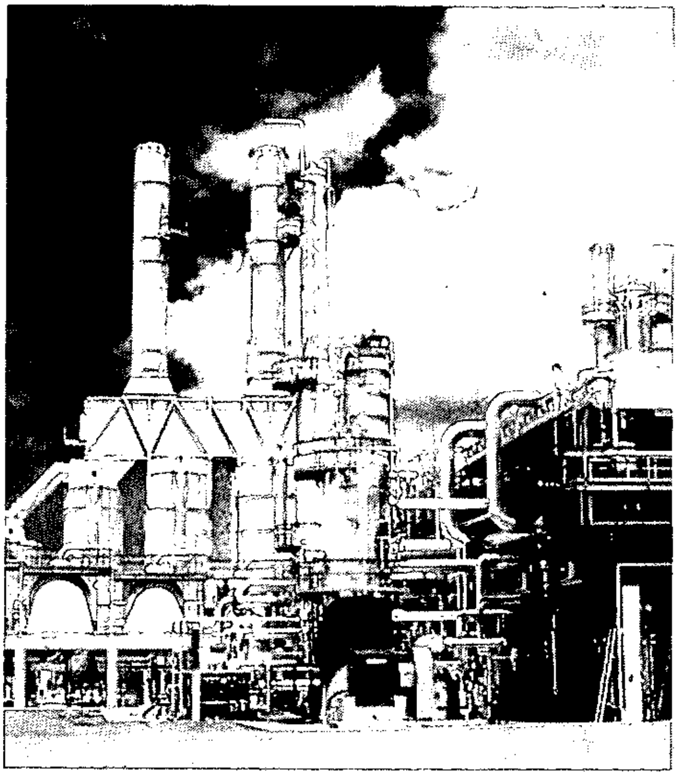
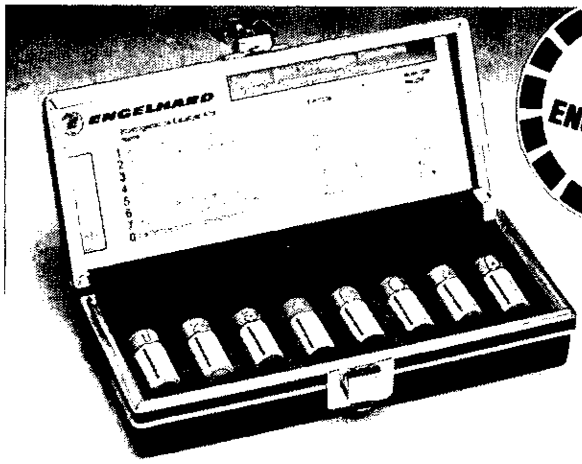
Catalyst evaluation kit





NEW FROM ENGELHARD

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Engelhard is now offering eight of the most popular homogeneous catalysts in convenient kit form. The kit, composed of Engelhard precious metal homogeneous catalyst compounds, is designed to enable the chemical researcher in greatly expanding his experimentation. A small sampling of the wide variety of Engelhard catalysts, the kit is an excellent introduction to the quality which earned Engelhard its reputation throughout the industry. This valuable kit is now available to you for a nominal price.

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244 Oxford Terrace Christchurch
Tel 63-240 Tx 4025

For further information circle 7 on Reader Reply Card

PRODUCT NEWS

NU CON FEEDERS

Nu Con Ltd is introducing three different feeder systems to New Zealand.

'Loss in weight' feeding is ideal for low rate applications requiring high accuracy or high rate applications for materials that cannot be handled by belt feeders. With feed rate capabilities down to 100ms per hour, the feeders are often used for the addition of critical ingredients in food or chemical processors.

For high feed rates of up to 23,500 kg per hour for such materials as fine powders 'loss in weight' twin screw feeding is ideal.

Another suitable application is when materials require containment to control dusting or prevent contamination.

In 'loss in weight' feeders, material travels from the refill system into the storage hopper, through the metering device and on downstream with no chance for the material to escape. This is especially critical in food or pharmaceutical applications or when handling toxic materials.

Free flowing and granular products are fed by single screws, while floodable materials are held under control and hard to flow materials are pumped by intermeshed twin screws.

Liquids and slurries can also be precisely fed under 'loss in weight' control when metering pump accuracy is not sufficient. The holding tank is fixed on the scale and the pump can be mounted either on or off the scale.

As part of an extensive diversification programme, Nu Con Limited is introducing a highly versatile range of American manufactured weigh belt equipment to mate with its existing component systems.

K-Tron's product line of weigh belt equipment can regulate dry bulk materials flow by weight (feeders), totalized mass throughput of material flow (meters), or deliver discreet quantities of bulk material (batchers).

A volumetric feeder is normally used to feed materials into a process where high degrees of accuracy are unnecessary and the material being fed is relatively free flowing and consistent in density.

K-Tron offers various models of two major types of volumetric feeders, single screw and twin screw.

Further information from Nu-Con, Penrose Ak. or by circling **23** on the reader reply card.

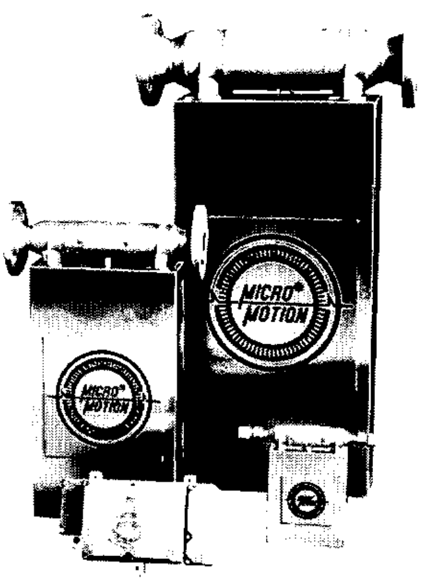
MASS FLOWMETERS

The American company which has become well known for its mass flowmeters has established a branch in New Zealand.

Micromotion could see the potential for mass flow metering in this country and has set up a local branch to service existing clients and establish new markets.

Most of the existing meters are used in CNG dispensers for filling automobiles. The mass based system overcame the difficulties associated with volumetric measurement and the corresponding pressure and temperature corrections.

The other major usage has been in the dairy industry predominantly for the measurement of cream. As cream has a proportion of entrained gas it has been a difficult product to measure by volumetric means. The Micromotion meter, being mass based gives the mass or weight of cream and so is unaffected by the entrained air.



A big advantage for industry is that the meters sensor tubes are made from stainless steel and have no moving parts which means they are easy to clean.

In other parts of the world such diverse products as molasses, cryogenic products, slurries, yeast, asphalt, hamburger meat, polypropylene and steam are being monitored by this method.

The new D series meter will be promoted in New Zealand. This has an hermetically sealed, stainless steel sensor housing which can be installed directly into any process or pipeline. The meters are intrinsically safe and the Remote Electronics can be located up to 150 meters from the Sensor. The Non-intrusive mass flow measurement of gases, liquids and slurries from .05 kg/min to 10 tonnes per minute is independent of changes in fluid density, viscosity, temperature or pressure.

For additional information contact Micromotion Australia Ltd or circle **24** on the reader reply card.

BECKMAN ELECTRODE

Futura II Star-Series Refillable Combination Electrodes are designed for demanding pH measurement situations, including those in which ionic strength is low such as acid rain and drinking water, temperature varies substantially or in samples which are sensitive to silver. The electrodes, available from Beckman Instruments, Inc., provide high performance in applications in which pH measurements are critical.

Star-Series electrodes, which operate in the pH range of 0 to 14, are accurate to ±0.01 pH. Response time in pH 4 to pH 7 buffer at constant temperature is stable to ±0.02 pH in 30 seconds. For temperature changes from 25°C to 75°C in pH 4 buffer, response is stable to ±0.02 pH in 30 seconds. Slope is 97 to 100 per cent, temperature range is −5 to 100°C, isothermal point is 7 pH and stability is ±0.002 pH for 24 hours.

Star-Series electrodes are available in glass or epoxy bodies. NZ agents Alphatech Systems Ltd, circle **25** on the reader reply card.

VULCATHENE CHEMICAL WASTE

A complete corrosion resistant plumbing system which embraces laboratory bench items such as wastes, drip cups and sinks, plus an impressive range of pipe fittings from 38mm up to 102mm is available ex stock from Insapipe Industries Limited in Auckland.

Vulcathene mechanical pipe fittings are robustly constructed with component parts injection moulded in black polypropylene, the mechanical jointing technique is simple in concept and fast to execute, capable of being undone and remade many times without affecting the joint's efficiency.

The Vulcathene mechanical plumbing system has been designed for the safe conveyance of low pressure chemical effluence, which makes it an ideal choice for schools, hospitals and industrial laboratory waste installations.

For further information circle **26** on the reader reply card.

CENTRIFUGE TUBES AND BOTTLES

Watson Victor Ltd are the agents for Nalgene centrifuge tubes and bottles with sealing cap assemblies.

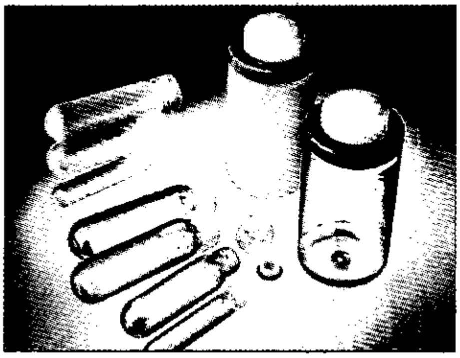
Materials

Polycarbonate (PC) is transparent and autoclavable, with excellent mechanical strength. Can be used in both refrigerated and non-refrigerated centrifuges.

Polysulfone (PSF) is autoclavable and transparent, with a straw-coloured cast. It's much more resistant to acids and bases than PC, and has higher purity for critical applications. Can be used in refrigerated and non-refrigerated centrifuges.

Polyallomer (PA) may be autoclaved repeatedly and is chemical resistant to acids, alcohols, aldehydes, bases, esters, aliphatic hydrocarbons and ketones. It withstands forces up to 50,000 x 6 and is the material of choice for high-speed use in refrigerated centrifuges (down to −40°C). Ideal for cold extractions of nucleic acids.

Polypropylene (PP) is translucent and has many of the same properties as PA. It is suitable for non-refrigerated centrifuges but is not recommended for refrigerated centrifuges.



Tubes

Choice of four sizes: 10, 28, 30 and 50 mL. Other manufacturers offer only 10, 16 and 50-mL sizes.

Three materials are available: PC, PSF and PA. Competitors offer only PC and PP.

Can be used up to 50,000 x g.

Bottles

250-mL capacities

Three materials: PC, PP and PA.

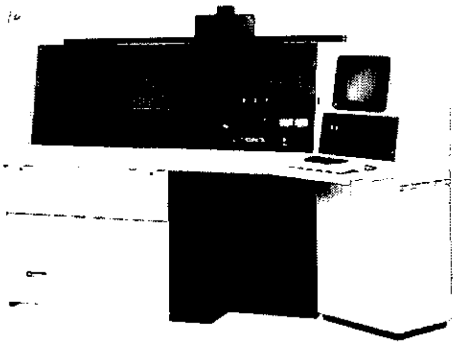
With Sealing Cap Assemblies, can be used up to 27,500 x g.

For further information, circle **27** on the reader reply card.

PRODUCT NEWS

ICP FROM KONTRON

Chemistry in New Zealand apologises for omitting Kontron's Plasmakon S35 ICP from its list of ICP instruments in the October issue. The Plasmakon S35 can be supplied as a combination sequential — simultaneous system. The simultaneous system will analyse up to 48 elements and background correction close to the peaks is possible. The sequential system incorporates an angle encoder which establishes the instantaneous grating position and the corresponding wavelength.



New Zealand agents are Roche Products (NZ) Ltd, further information can be obtained by circling **28** on the reader reply card.

ELDEX PUMPS

Alltech New Zealand have been appointed distributors for the range of precision equipment for HPLC manufactured by Eldex Laboratories Inc, of San Carlos, California.

Eldex Pumps, in particular, are noted for their reliability and economy of price, as well as having synchronous motors, which do not vary in speed with line voltage fluctuations.

A fully descriptive brochure (#411) is available from Alltech New Zealand, by circling **29** on the reader reply card.

TSK COLUMNS FOR HIGH PERFORMANCE PROTEIN CHROMATOGRAPHY

Sci-Med (NZ) Ltd wishes to announce the availability of the new TSK-Phenyl 5-PW Hydrophobic Interaction Chromatography Columns especially developed for protein HPLC.

The new support has been developed by introducing phenyl groups by way of an ether linkage into TSK-Gel G5000PW which is a hydrophobic-polymer-based material of large pore size.

This packaging exhibits a mechanism similar to reversed phase but without the attendant disadvantages of denaturation (and loss of biological activity) due to high concentrations of organic solvents used in conventional RPLC.

For reprints of a recent JOURNAL OF CHROMATOGRAPHY article detailing the performance and characteristics of this new packing, please contact Sci-Med (NZ) Ltd or circle **30** reader reply card.

HPLC COLUMNS

The MN Cartridge System for HPLC is based on a short column (100mm) and a guard column (30mm) which can be coupled easily by means of a union. They are then ready for use. The system is versatile as to combination of analytical and guard column as well as the number of columns. Further advantages include, short analysis times, maximum column life, reduced solvent use, and connections without tools. Made by Machery-Nagel of West Germany, the MN Cartridge System is available only through Alltech New Zealand.

A descriptive brochure is available by circling **31** on the reader reply card.

HOLLOW CATHODE LAMPS

Photron Pty Limited have announced a range of high intensity hollow cathode lamps for use with atomic absorption and atomic fluorescence spectrophotometers. Improved performance is achieved by passing a secondary boost discharge through a cylindrical cathode. Adjustment of the boost discharge optimizes exitation for a particular sputtering current, thus removing the cause of self absorption, which is the limited factor in most conventional lamps.

"Super Lamps" are not only more intense than hollow cathode lamps, but in most cases more sensitive.

Lamps are available for all the usual AA elements except for Ga, In, Hg, Sr and H. Several multi-element lamps are available too.

For further information, please contact Advanced Electronics Limited, or circle **32** on the reader reply card.

SEQUOIA-TURNER MODEL 390 SPECTROPHOTOMETER

The Model 390 offers analysts extremely high spectrophotometer performance at very reasonable cost. Four models of operation are switch selectable and include Concentration and Factor modes as well as Absorbance and Percent Transmission.

The monochromator on the Model 390

PRODUCT NEWS

consists of a plane diffraction grating in an f7 Ebert mounting with first surface reflective optics. This design ensures efficiency and gives the Model 390 a continuous wavelength range of 330nm to 1000nm to cover most routine U.V. and colorimetric tests. This range can be expanded to 210nm with the Far UV accessory.

Advanced electronics include a solid state silicon photo detector and integrated circuit analog and digital processing. With an 8nm bandwidth, the Model 390 provides greater sensitivity than comparably priced instruments. The combination of this narrow bandpass and less than 0.5 percent stray light produces exceptional photometric linearity. Performance is further enhanced with a wavelength accuracy within 2nm over the full range.

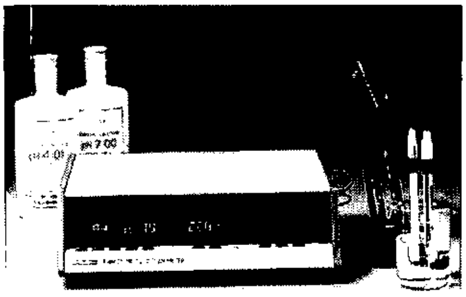
Functional design makes the Model 390 one of the simplest spectrophotometers in the world to use. A large LED display provides easy readability. With a simple turn of a knob, the readout can be switched between modes and the controls are arranged in the order they are used.

With the Sequoia-Turner Instafill accessory, the Model 390 will perform automatic sampling for rapid throughput.
Full details and specifications can be obtained from Kempthorne Medical Supplies Ltd or by circling 35 on the reader reply card.

NEW MICROPROCESSOR-CONTROLLED pH METER

Radiometer has introduced the PHM85 Precision pH Meter for research and high-precision measurement of pH, pX, mV and temperature. The resolution is 0.001 pH, 0.001 pX, 0.1 mV and 0.1°C.

The buffer values can be selected as desired and are easily keyed in and stored in the microprocessor's memory.



A 20-character alphanumerical display assists in prompting with clear and concise directions. The operator is kept up-to-date on electrode performance, as the sensitivity, zero-point and ISO-pH point are automatically calculated and displayed during calibration. All calibration data can be recalled for checking by the simple press of a key.

PHM85 has RS-232C output for connection to computer or printer.

Routine work can be automated because PHM85 can be connected to a sample changer for automatic measurement of up to 20 samples in series. When connected to an automatic burette, the PHM85 controls automatic end-point titrations.
N.Z. Agents, Watson Victor Ltd, circle 36 on the reader reply card for further information.

RHEODYNE INC.

In the October issue of Chemistry in New Zealand an article was published in Product News from which it may have been possible to infer that Rheodyne Inc had appointed a sole agent in New Zealand. In fact Rheodyne does not grant exclusive agencies and is represented by three companies in New Zealand.

RATHBURN HPLC SOLVENTS

Sci-Med is pleased to announce their association with a highly respected UK manufacturer of HPLC grade solvents. As of January 1985 Sci-Med will be holding stocks of commonly requested solvents as Methanol and Acetronitrile.

In addition, Rathburn supply a complete range of solvents for HPLC as well as Glass Distilled Grade Solvents and Sequencer Grade Materials.

Sci-Med will be pleased to quote on your bulk order requirements at competitive prices.

For further details such as specifications and prices, contact Sci-Med or circle 37 on the reader reply card.

TWO GELS FROM PIERCE

Pierce Chemical Company has just announced a new affinity chromatography gel for the removal of detergents from protein solutions. Extracti-Gel D is an exclusive product from Pierce and has high detergent binding capacity over a broad range of pH and buffer compositions.

According to the Marketing Manager for BioResearch Products, "detergents are trapped within the porous gel matrix while proteins greater than 10,000 molecular weight are excluded and recovered in very high yields."

Extracti-Gel D is suited for both column and batch techniques. A packed column can be used repeatedly until capacity is reached, then regenerated and used again.

The binding properties for Extracti-Gel D have been determined for CHAPS, SDS and Triton X-100. However, Extracti-Gel D will be effective for removing all detergents common to protein purification schemes. Extracti-Gel D is available in convenient 10 ml and 100 ml quantities.

For further information, circle 38 on the reader reply card.

Pierce Chemical Company has also announced the availability of Excellulose GF-5, a pre-swollen gel filtration support for desalting solutions containing macromolecules. Excellulose GF-5 is a cross-linked beaded cellulose with an exclusion limit of 5000 daltons.

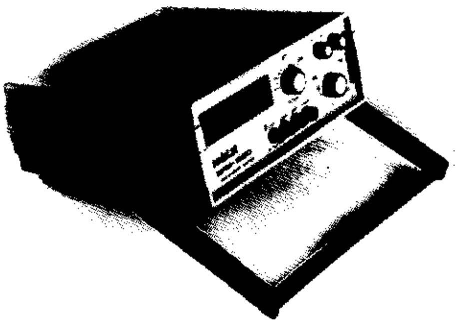
Macromolecules, with a molecular weight greater than the desalting gel's exclusion limit pass around the beads and are eluted in the column's void volume. Smaller molecules penetrate the pores of Excellulose beads and are eluted in one column volume. Excellulose GF-5 may be reused after the low molecular weight compounds have been removed. Excellulose GF-5 is also suitable to fractionate small molecules. Polyethylene glycols, with a molecular weight of 400 to 5000 have been successfully separated using this support.
NZ agents Labsupply Pierce (NZ) Ltd, circle 39 on the reader reply card for further information.

pH METER FROM SOLSTAT

The top of the range meter from the SOLSTAT stable is the totally versatile EPM 1500 digital electrometer type instrument categorised for operation as a pH/mV/SI Meter.

Fully solid-state circuitry is employed throughout, and high quality, low-drift components in critical areas ensure excellent stability and reproducibility over the range of the instrument, and over a wide ambient temperature range, Monolithic dual FETS in the front end ensure the highest possible input impedance with lowest temperature dependance, offset and linearity.

Digital reading allows 0.001pH or 0.1mV resolution directly over the entire instrument range, and control functions are automatically made redundant when the mode of operation so requires.



System design includes provision for BCD data output if required, and analogue data is available as standard. A RUN/HOLD facility permits locking of the display to the last reading.
Detailed specifications can be obtained from the distributors, Kempthorne Medical Supplies Ltd or circle 40 on the reader reply card.

HEATED STERILE VENT FILTERS FOR FERMENTATION VESSELS

Ultrafilter of Dusseldorf, have introduced a new steam jacketed sterile filter specially designed for venting fermentation vessels.

Because fermenter air is usually 100 per cent saturated with water vapour, sterile vent cartridges in unheated filters can become contaminated by micro-organisms. To maintain the effectiveness of the cartridge, it is desirable to reduce the saturation of the vent air to 70 per cent by heating.

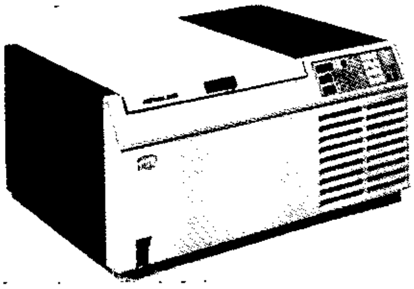
The Ultrafilter steam jacketed filter vessel is designed to operate on a 120 deg C steam supply. The heating action typically increases vent air temperature from 30 deg C at inlet to 60 deg C at outlet.

The steam jacketed sterile filters are used extensively in vaccine production where it is important to prevent culture material escaping into the atmosphere. Other users include the fermented foods, pharmaceutical, wine and brewing industries.
NZ agents, FRAM (NZ) Ltd, circle 41 on the reader reply card for further information.

NEW PRODUCTS

BENCH-TOP REFRIGERATED CENTRIFUGE

To be introduced to New Zealand in March, 1985 is the latest addition to MSE range of centrifuges; the Mistral 3000, a large capacity bench-top refrigerated machine which features micro-processor control.



Offering a 3 litre capacity (4 x 750ml wind-shielded swing-out rotor) the Mistral 3000 has a true refrigeration system which gives full control over the range 0°C to 30°C with any rotor at any speed. Top speed is 6000 rpm and a full 3 litre load can be run at 3660 rpm, giving a maximum RCF in excess of 3000g. The brushless induction drive unit is of the type normally found only in more expensive floor-standing machines.

A series of demonstrations throughout the country is being planned. Should you wish further information or a demonstration, please contact Kempthorne Medical Supplies Ltd, or circle **42** on the reader reply card.

PEL TEMPERATURE WORKSHOP

The Temperature Standards Section of the DSIR's Physics and Engineering Laboratory is preparing for a one-day temperature workshop to be held at PEL on 19 February.

Most industrial processes involve temperature changes and accuracy here can be vital to the quality of the final product.

The workshop is being designed especially for users of temperature monitoring equipment, and will concentrate on the use of temperature sensors and how to get reliable results.

The Temperature Workshop in February will help those using temperature sensing equipment improve the accuracy of their measurements, and so avoid the risks of costly breakdowns.

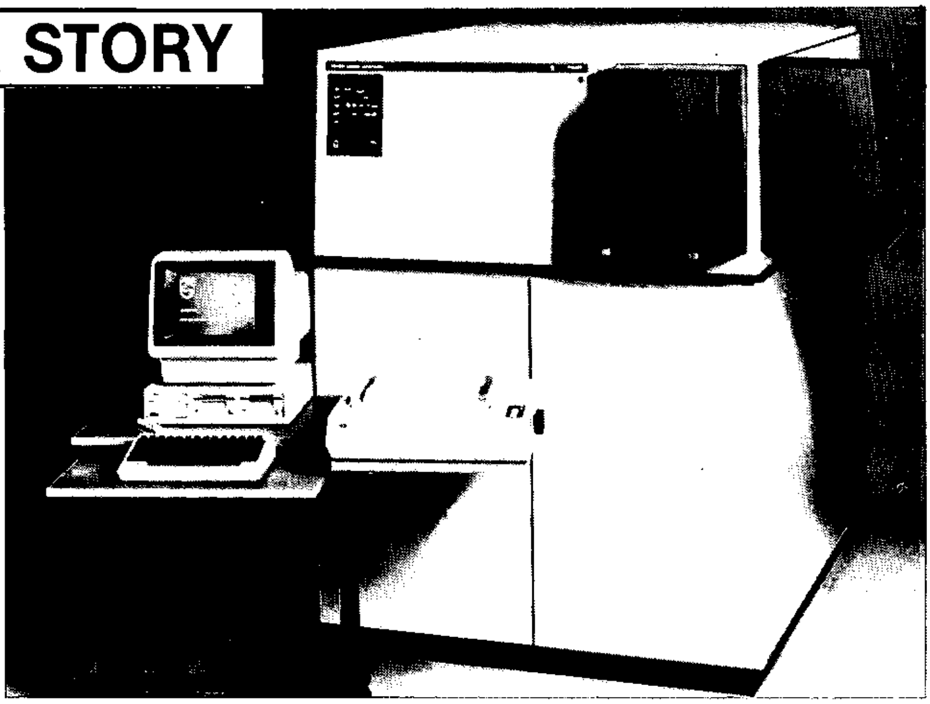
Making the ice point for checking thermometers is an essential technique all thermometer users should be able to do.

A back-up text 'Traceable Temperatures' will be provided at the workshop together with course notes.

Those interested in attending this workshop should contact John Nicholas at the Physics and Engineering Laboratory, DSIR, Private Bag, Lower Hutt.

Depending on the demand, other workshops can be arranged.

FRONT COVER STORY



With dual excitation positions and a range of interchangeable excitation stands, the Philips PV 8050 Series emission spectrometer system offers great versatility to handle wide-ranging workloads.

Philips launches high-performance optical emission range

The PV 8050 Series of optical emission spectrometers from Philips Analytical is available in a choice of configurations optimised for different applications of conventional electrical discharge and inductively coupled plasma excitation.

All are microprocessor-controlled, and can be used with either DEC or Hewlett Packard computers for data processing.

New hardware features

Systems are based on high precision optics, which can be equipped for simultaneous measurement of up to 56 elements in the wavelength range 165 - 485 nm. An additional Monk-Gillieson monochromator may be fitted into the temperature- and pressure-controlled optical enclosure, giving access to longer-wavelength lines of particular value in aluminium analysis and ICP work. All lines are measured in the first order, ensuring high intensities and minimal background.

Flexibility is further increased by a programmable scanning channel option — used to explore spectral zones or to measure specific wavelengths for which fixed exit slits are not provided.

Innovative features include a rigid exit slit plate, carrying individually selected slits for given applications, and light guides to eliminate cross-talk between adjacent photomultiplier detectors. These enable very closely spaced wavelengths to be measured, and avoid the need for compromise in line selection.

A low pressure argon atmosphere allows elements such as C, S, P, and B to be determined using their preferred short wavelength lines. It also provides independence from external pressure variations, while permitting economical operation.

Choice of models

Versions include the PV 8050 fitted with a single excitation stand, and the PV 8055 dual excitation stand model. Both are designed for use with the Philips range of excitation sources, including the 500 - 500 Hz multi-frequency triggered capacitor discharge unit — which offers the fastest method available for metals analysis. Plug-in excitation stands enable a variety of sample types to be handled.

The PV 8060 is a dedicated ICP system incorporating a high performance source unit based on the design of Dr Boumans. With constant focus achromatic entrance optics and easy height adjustment, it allows full exploitation of this versatile technique for the analysis of liquids and solutions.

For laboratories with wide-ranging workloads, the PV 8065 is equipped for both electrical and ICP excitation. It is thus possible to analyse liquid and solid samples with a single instrument. Accessories are available for automatic background correction and sample handling.

Advanced software

All systems benefit from new generation software that combines powerful data processing capability with maximum ease of operation. Measuring programmes are assembled with the aid of self-explanatory dialogues via a keyboard terminal — and routine analysis can be undertaken by personnel with no special analytical or computer skills.

Extensive data treatment and display capabilities are included to meet the needs of more experienced users.

Further information from: Philips Electrical Industries of N.Z. Limited
or by circling **43** on the reader reply card.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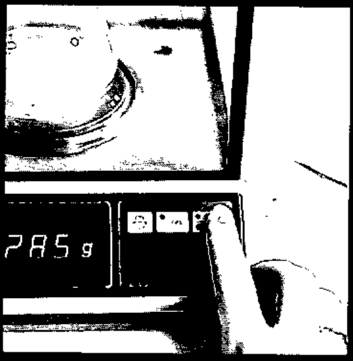

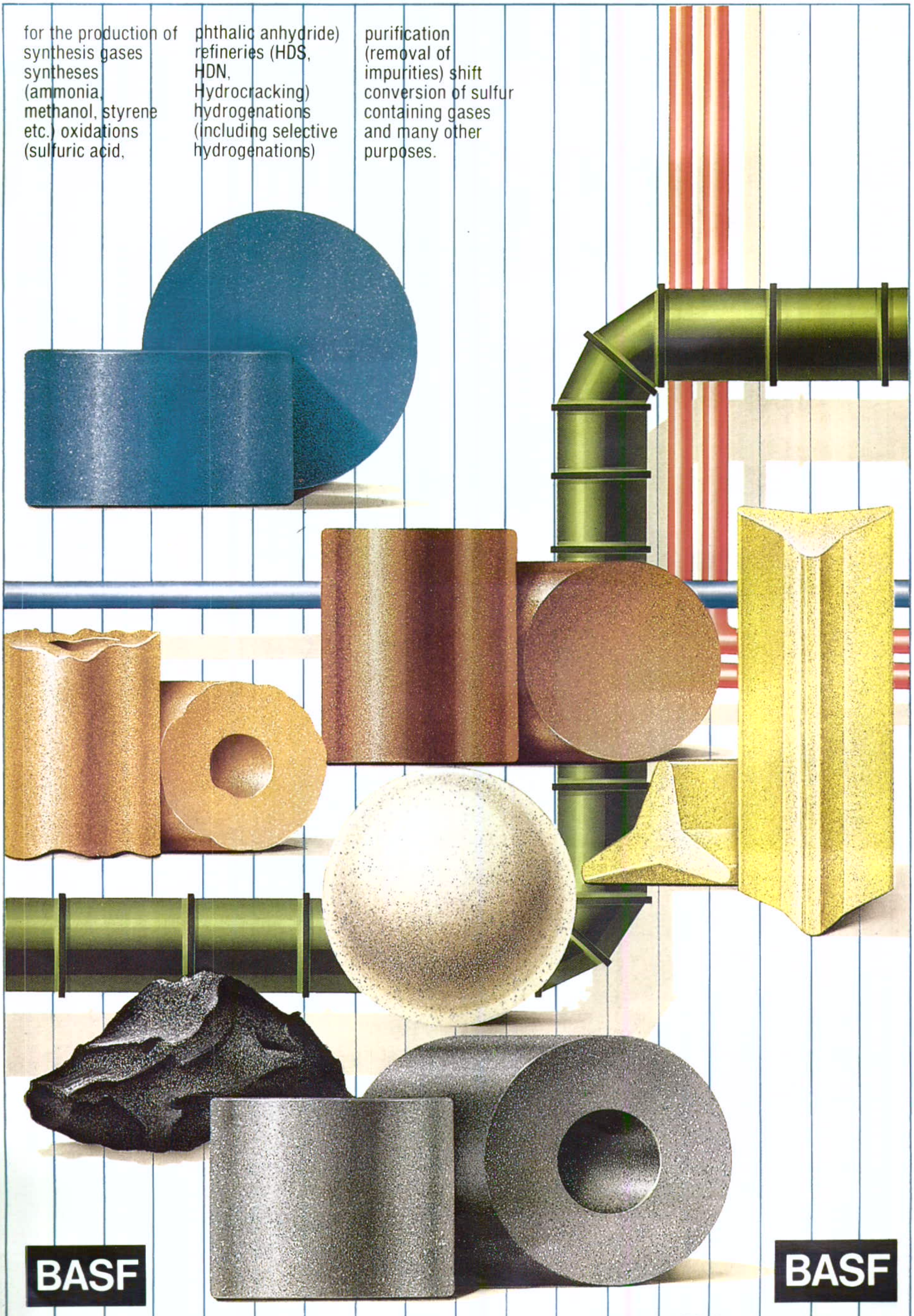

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