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REVIEW

A brief history of organometallic chemistry in Australia and New Zealand

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The Danish pharmacist, Zeise, reported the first documented transition metal organometallic compound, Zeise's salt, in 1827. In 1953, 126 years later, **D. P. Mellor** and **J. A. Wunderlich**, at the University of Sydney, completed the crystal structure determination of Zeise's salt, $K[PtCl_3(C_2H_4)].H_2O$.[1] This review traces the development of organometallic chemistry in Australia and New Zealand from the arrival of Eustace Turner at the University of Sydney in 1919.

The development of the closely related subject of coordination chemistry in Australia has been reviewed recently.[2] Although Australia's oldest university, the University of Sydney, was founded in 1850, the first Ph.D. degree awarded by an Australian University was conferred by the University of Melbourne in 1948, and the inorganic chemist Nora Gyarfas was awarded one of the first two Ph.D. degrees from the University of Sydney in 1951. Now, most Australian and New Zealand universities have at least one Department or School of Chemistry. In addition, both Australia (Commonwealth Scientific and Industrial Research Organization, CSIRO) and New Zealand (Department of Scientific and Industrial Research, DSIR) have government-run research organizations.

This review sketches the growth of Australian and New Zealand organometallic chemistry, its relationship to coordination chemistry in the region, and the stimuli that influenced many antipodean researchers. The coverage must of necessity be selective, and so is limited to the practice of organometallic chemistry in Australia and New Zealand, and ignores many of the contemporary practitioners, some of whom have their work represented in this collection. The order of presentation reflects a mixture of chronology, genealogy and geography.

EARLY YEARS AND THE UNIVERSITY OF SYDNEY

In 1919 Eustace Turner (1893–1966) and George Burrows (1885–1950) were appointed Lecturers in Chemistry at the University of Sydney. This was to be the beginning of organometallic chemical investigations in Australia. During the First World War, Turner worked as a Research Assistant to Professor W J Pope in Cambridge. Pope was a member of the Chemical Warfare Committee, and he and Turner investigated the synthesis of arsines. This work on triphenylarsine and diphenylarsinous salts was published in 1920.[3] In Sydney, Turner and Burrows began a collaborative research effort on the chemistry of nitroprussides, and on arsenic chemistry. This collaboration produced addition compounds of the type $R_1R_2R_3As.RAsI_2$,[4] the first optical resolution of arsenic compound—the (±)-benzylmethyl-(α-naphthyl)-phenylarsonium ion[5]—and the isolation of $PhMe_2As.MI_3$ ($M = P$, As, Sb, Bi), $[PhMe_2As]_2.SnI_4$, $[PhMe_3As]_2[CdI_4]$ and $[PhMe_2EtAs][MI_3]$ ($M = Hg$, Pb).[6]

This work represented the first investigations on arsine metal compounds performed in Australia. Turner returned to England in 1921, after only two years, but left behind a significant legacy to the development of organometallic chemistry in Australia. Burrows resumed work on metal arsine complexes in 1933, and published a series of papers which described the isolation and characterization of the complexes $[Ag(Ph_2MeAs)_2]X$ ($X = Cl$, Br, I); $[Cu(Ph_2MeAs)X]$ ($X = Cl$, Br, NO_3), $[Cu(PhMe_2As)X]$ ($X = Br$, I); $[Cu(PhMe_2As)_2]X$ ($X = Cl$, Br); $[Pt(Ph_2MeAs)_2Cl_2]$ and

$[Pt(PhMe_2As)_2X_2]$ ($X = Cl$, Br); $[Zn(R_3As)_2X_2]$ ($R_3As = Ph_2MeAs$, $PhMe_2As$; $X = Br$, I); $[(PhMe_2As).ZnCl_2]$, $[(R_3As).CdX_2]$ ($X = Cl$, Br, I); $[Hg(R_3As)_2X_2]$ and $[(R_3As).HgX_2]$ ($X = Cl$, Br, I).[7–15] Much of this work is reviewed in Burrows' Royal Society of New South Wales 1940 Liversidge Lecture, 'Organic arsenicals in peace and war'.[16]

NYHOLM AND BIRCH

In 1937, Ronald (later Sir Ronald) Nyholm (1917–1971) worked for his B.Sc. (Hons.) degree at the University of Sydney under the supervision of Burrows on a project devoted to metal–arsine complexes. Nyholm's contemporaries included **Arthur Birch** (B.Sc. 1937), **John (later Sir John) Cornforth** (B.Sc. 1938), and **Rita Harradene (later Lady Cornforth)** (B.Sc. 1937).

Burrows retired because of ill health in 1941. In England, meanwhile, Turner had become a Senior Lecturer in Chemistry in the East London (later Queen Mary) College in 1923. One of his first research students was Raymond J. W. Le Fèvre, who was Professor of Chemistry at the University of Sydney from 1946 until 1970.

Ronald Nyholm joined the chemistry staff of the Sydney Technical College in 1942. He quickly formed a collaboration with Frank Dwyer, investigating Rh(II) and Rh(III) complexes of arsines and other ligands.[17–26] Compounds formulated in these 1940s papers as Rh(II) dimers, $[RhX_2(Ph_2MeAs)_3]_2$ ($X = Cl$, Br, I), were shown in 1960 to be Rh(III) hydrides.[27] Several arsine complexes of iridium, formulated as $[IrX_3(Ph_2MeAs)_2]_2$, $H[IrX_4(Ph_2MeAs)_2]$ and $[IrX_2(Ph_2MeAs)_3]_2$ ($X = Cl$, Br, I) were also reported by Dwyer and Nyholm.[28,29]

Nyholm left Australia in 1947 to take up an Imperial Chemical Industries Fellowship, working with Professor Christopher (later Sir Christopher) Ingold at University College, London. He obtained his Ph.D. in 1950 for his work on metal arsine complexes, and became a Lecturer at University College that year. Nyholm returned to Australia in February 1952, to an appointment at the School of Chemistry, University of New South Wales. His stay in Australia was relatively short—he returned to University College, London in 1955 as a Professor. However, during those three years, Nyholm's influence on the development of Australian Inorganic Chemistry was established. Stanley Livingstone, Ray Martin, Brian Figgis and Brian Gatehouse were all contemporaries of Nyholm.

Arthur Birch is one of Australia's most distinguished chemists. He was born in 1915, and was educated at Sydney Technical High School. Birch had a gifted teacher who had obtained a B.Sc. (Hons.) degree from the University of Sydney working with George Burrows, and who stimulated Birch's interest in chemistry by displaying several beautifully crystalline samples of Werner complexes that had been prepared by Burrows. Birch graduated from the University of Sydney with a B.Sc. (Hons.) degree (First Class) and shared the University Medal with Rita Harradene in 1937. As an undergraduate vacation student Birch worked briefly with Burrows on copper–arsine complexes, gaining some early exposure to organometallic chemistry which was to prove useful later. He completed an M.Sc. at the University of Sydney in 1938, under the supervision of Frank Lions, and then travelled to the Dyson Perrins Laboratory, Oxford, as an 1851 Exhibitioner. Birch completed his D.Phil. ('Fatty acids of the tuberculosis bacillus') in 1940 under the supervision of Sir Robert Robinson (Professor of Chemistry at the University of Sydney, 1913–1916), and spend the War years as a Research Fellow at the Dyson Perrins Laboratory, remaining there as an ICI Fellow until 1948. During this period, he developed the powerful and versatile method of reduction of aromatic rings by solutions of sodium in liquid ammonia or other amines, now known as the Birch reduction.[30] The method rapidly passed into general use, its most famous application being in the synthesis of the first oral contraceptive. Although developing general ideas, Birch's subsequent organometallic work has been based largely on metal complexes of Birch reduction products of aromatic compounds. The Birch reduction of substituted benzenoids made a variety of prochiral substituted cyclohexa-1,4- and, hence, −1,3-dienes readily available. These could be activated towards highly stereoselective syntheses by complexation with the $Fe(CO)_3$ moiety.

In 1949, Birch moved to Cambridge as a Smithson Fellow of the Royal Society. He returned to the University of Sydney in 1952 as Professor of Organic Chemistry, and accepted the Chair of Organic Chemistry at the University of Manchester in 1955. Whilst at Manchester, Birch examined some arene π-complexes of chromium, molybdenum and tungsten (including $[(\eta^6\text{-steroid})M(CO)_3]$ complexes of the type described elsewhere in this issue.[31,32] $[(\eta^6C_6H_6)Cr(CO)_3]$ was produced in 82% yield by refluxing $Cr(CO)_6$ and 1-methoxycyclohexa-1, 4-diene in *n*-nonane. The diene was prepared by the Birch reduction of anisole, the overall procedure providing a useful method for the removal of methoxy groups from aromatics. In 1963/1964, work on $[(\text{cyclohexa-1,3-diene})Fe(CO)_3]$ complexes started in Manchester in collaboration with Jack Lewis.[33,34] Another Australian, Bruce Wild, was also involved in this collaboration. Birch and Wild were both later to join the Research School of Chemistry, ANU. Birch's group also prepared $Fe(CO)_3$ adducts of vitamin A and of the opium alkaloid thebaine, in which the $Fe(CO)_3$ group was coordinated to a diene functionality.[35–37] Birch's organic strategies needed pure samples of conjugated cyclohexadienes. Unfortunately, although the Birch reduction readily yielded unconjugated cyclohexadienes which could be equilibrated with their conjugated isomers, pure samples of the latter were not easily prepared. Pettit (coincidentally, another Australian) had shown that both conjugated and unconjugated cyclohexadienes gave the $[(\text{conjugated diene})Fe(CO)_3]$ complex, from which the conjugated diene could be released.[38] Birch attempted this reaction with 1-methoxy-cyclohexadienes and obtained a mixture of substitution isomers of the $[(\text{diene})Fe(CO)_3]$ complex. The direct separation of these isomers was not developed until later, but the conjugated diene could be liberated by selective oxidation. Birch observed that hydride abstraction from the $[(\text{diene})Fe(CO)_3]$ complexes gave both $[(\text{dienyl})Fe(CO)_3]^+$ and $[(\text{dienone})Fe(CO)_3]$, which led him to consider further synthetic uses, and the general philosophy of 'lateral activation'.

Birch's exploitation of the $Fe(CO)_3$ group in organic synthesis developed predominantly following his return to Australia in 1967, when he accepted an invitation to become Foundation Professor of Organic Chemistry and Foundation Dean of Chemistry in the Research School of Chemistry at the Australian National University. Birch showed that a variety of $Fe(CO)_3$-containing derivatives react readily with conjugated cyclohexa-1,3-dienes to yield $[(\text{cyclohexa-1,3-diene})Fe(CO)_3]$ complexes. The $Fe(CO)_3$ group protects the diene system during subsequent reactions of the organic ligand.[39–41] Alternatively, Birch and Haas reported the ready preparation of $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]^+$ cations from the neutral dienes in 1968.[42] This class of cation had first been prepared by Fischer.[43] The importance of the $[(\text{cyclohexa-1,3-diene})Fe(CO)_3]^{+/0}$ derivatives in organic synthesis lies in their ready preparation from easily available reagents, the necessarily *cisoid* structure of the complexes, the activation of the dienes to facile chemical conversions, the chirality induced in prochiral substituted dienes by complexation, and the highly stereospecific reactions undergone by the complexed diene. Most of this chemistry, and the associated isomerizations of the dienes and diene complexes,[44] the resolution of the chiral diene complexes,[45–48] chiral transfer of the $Fe(CO)_3$ group,[49,50] the philosophy of lateral control of structure and reactivity,[51,53] and the perspective of 'inorganic enzymes'—whereby transition metal atoms act as assembly and control centres in organic synthesis[54,55]—has been developed by Birch, and been exploited by him in the synthesis of the enzyme inhibitor gabaculine in resolved form with known absolute configuration, and in the synthesis of fully resolved shikimic acid from both enantiomers of a benzenoid precursor.[56,57]

Arthur Birch was elected a Fellow of the Royal Society and a foundation Fellow of the Australian Academy of Science (1954); he was the first Australian to be elected to Full Foreign Membership of the USSR Academy of Science (1976), and to be awarded the Davy Medal of the Royal Society (1972). He was Chairman of the Australian Government's independent inquiry into the CSIRO (1977), which recommended far-reaching changes to the structure and function of the CSIRO. Arthur Birch retired in 1980 and is currently a Professor Emeritus and ANU Fellow at the Australian National University.

The foregoing has been restricted to Birch's contributions to organometallic chemistry. His versatility and impact are emphasised by his even more extensive contributions to natural-product and biological organic chemistry, his fundamental discoveries in steroid chemistry which led directly to syntheses of sex hormones, the corticoid hormones and oral contraceptives, and the enunciation of his 'acetate (polyketide) hypothesis'.

John Pinhey graduated B.Sc. (Hons.) with a University Medal in 1956 and Ph.D. in 1959 from the University of Sydney, where he worked under the supervision of the late E. Ritchie on structure determination in the alkaloid field. In September 1958, Pinhey moved to Imperial College, London, where he remained until early 1961. During this period he worked as a Postdoctoral Fellow, and later Assistant Lecturer, in Sir Derek Barton's research group studying the photochemistry of sesquiterpenoid cyclohexadienones. This stimulated his interest in organic photochemistry and terpenoid chemistry, and when he returned to Australia in 1961 as a Lecturer at the University of New England, he initiated research in both of these areas. In photochemistry, he has been involved in studies of rearrangements of aromatic ethers, α,β-unsaturated nitro compounds and cyclohexadienones, and the photoreduction of haloaromatics, whilst his terpenoid work has been mainly concerned with the production of steroids from readily available naturally occurring compounds. Pinhey moved to a Lectureship at the University of New South Wales in 1963, and then in 1965 to a Senior Lectureship at the University of Sydney, where he is now Reader in Organic Chemistry.

It was not until the early 1970s that Pinhey first entered the area of organometallic chemistry. This was quite unplanned, and resulted from the isolation of some aryllead(IV) triacetates during the investigation of the acid-catalysed oxidation of a number of halobenzenes by lead tetraacetate. An examination of these compounds revealed that they were remarkably efficient electrophilic arylating agents, especially of soft carbon nucleophiles. This rare and synthetically useful reactivity led Pinhey to make a detailed study of organolead triacetates, and this is now his major research interest. This work has led to the development of very general metal–metal exchange routes to aryl-lead triacetates, and the much less stable vinyl-lead and alk-1-ynyl-lead triacetates. Like the aromatic compounds, the latter compounds are electrophilic vinylating and alkynylating agents, respectively, and are being developed at present as new reagents for organic synthesis.

Mike Snow is another graduate of the University of Sydney. He completed his B.Sc. (Hons.) (1962) and M.Sc. (1964) degrees under the supervision of **Hans Freeman**. Snow obtained his Ph.D. in 1966, at University College London ('Carbonyl complexes of middle transition metals) for work on metal arene complexes under the supervision of R. S. Nyholm and M. H. B. Stiddard.[58,59] He took up a position as Lecturer in the Department of Physical and Inorganic Chemistry at the University of Adelaide in 1966. Much of Snow's recent work in organometallic chemistry has been devoted to the synthesis and characterization of fluorocarbonyls of manganese and rhenium, via bromide abstractions from $[M(CO)_xL_{5-x}Br]$ ($M = Mn$, Re; $x = 5,3$). This led to the isolation and characterization of some of the first fluorocarbonyls of manganese, an early example of an μ_3-F ligand, and a variety of monomeric and cluster species, such as $[Re(CO)_5(OH)_2)]^+$, $[Mn_4(CO)_{12-x}F_x(OH)_{4-x}]$ and $[Re(CO)_3F]_4$.[60-63] Recently, the precise low-temperature structure of $Becp_2$ was determined in collaboration with **Jim Beattie** of the University of Sydney.[64] Beryllocene provided an early example of 'ring slippage' in metallocenes. Mike Snow is currently a Reader (part-time) in the Department of Physical and Inorganic Chemistry at the University of Adelaide.

Merv Cooper worked with BHP Ltd in Newcastle, NSW, from 1945 to 1955. In 1952, he graduated A.S.T.C. from the Sydney Technical College, and in 1955 completed his B.Sc. (Hons.) degree under the supervision of W. F. Pickering at what was originally the Newcastle College of the University of Technology in Sydney. The University of Technology later became the University of New South Wales, and the Newcastle College of the University of Technology is now the University of Newcastle. Cooper's B.Sc. (Hons.) work was in ion-exchange chemistry, and, following a suggestion from Nyholm, then in London, Cooper undertook a part-time Ph.D. at Battersea Polytechnic under the supervision of J. E. Salmon. To finance his studies, Cooper worked from 1955–1957 with the Permutit Company in London on a variety of ion-exchange problems. At that time, Mary McPartlin was also working part-time at the Permutit Company while doing her early studies at Battersea. This was to be the foundation of a successful organometallic synthesis/structural collaboration in years to come. Merv Cooper spent 1957/1958 in Canada, working on uranium extraction with Ion-Exchange, Canada, Ltd, and returned to London as a Research Associate at Battersea Polytechnic, completing his Ph.D. in 1960. He was then appointed as a Research Officer, subsequently Senior Research Officer at the Australian Atomic Energy Commission (now the Australian Nuclear Science and Technology Organization), where he worked on the use of ion-exchange methods in the separation of uranium isotopes. In September 1963, Cooper moved to the University of Sydney as a Lecturer in Inorganic Chemistry, and continued his research into ion-exchange chemistry. Professor Gordon Stone, F.R.S., spent a period of study leave at the University of Sydney in 1965. As a Visiting Professor, Stone delivered a series of lectures on organometallic chemistry, which inspired Cooper to change his research direction to organometallic chemistry. Cooper began by incorporating the potentially tridentate pyridine-2-aldehyde ligand into metal carbonyl compounds to induce the ligand to become bidentate, and to undergo carbon–metal bonding. There followed a series of investigations into metal carbonyl complexes of other ligands such as β-diketones and monothio-β-diketones,[65] and the use of crown ethers to stabilize mononuclear and dinuclear anionic complexes of chromium, molybdenum and tungsten pentacarbonyls with the ligands HS^- and μ-HS^-.[66] Much of the structural work on these compounds was performed by Mary McPartlin at the Polytechnic of North London; she had obtained her Ph.D. in 1966, working on the X-ray crystallography of coordination compounds, at the University of New South Wales under the joint supervision of 'Blue' Barclay and Neville Stephenson. Cooper's later work was concerned mainly with the syntheses of gold clusters (including an Au_9 species), the synthesis of chelating P–N hybrid ligands, and the introduction to organometallic chemistry of the previous unused techniques of electric and magnetic birefringence.

The chemistry of the novel ligand (2-aminophenyl)diphenylphosphine proved to be quite interesting.[67–69] The facile de- and reprotonation of the coordinated nitrogen generated some unusual chemistry of the amido (imido) group in its monodentate and bridging modes.[70,71] Two of these ligands could be joined to form a tetradentate P_2N_2 ligand of interesting potential.[72]

Shortly before his retirement in July 1985, Cooper began a collaboration with **Manuel Aroney** and **Geoff Ritchie**, former students of Le Fèvre's, and also of the University of Sydney, into the applications of polarizability and birefringence measurements to organometallic chemistry. Notable results from this work were the measurement of the charge on the metal in ferrocene and in ruthenocene,[73] values not readily available by existing techniques, and investigations into the extent of Cr–L π-bonding in $[LCr(CO)_5]$ ($L = PMe_3$, NH_3, NMe_3) derivatives.[74] This 'direct' measurement of the delocalized component of, in particular, the Cr–P bond contrasts with the equivocal conclusions derived from other techniques, such as infrared spectroscopy. Cooper spent short periods at University College (1970/1971) and the Polytechnic of North London (1973/1974 and 1981) collaborating with Nyholm and with McPartlin, and now lives in retirement in the NSW coastal town of Tea Gardens.

THE ADELAIDE INFLUENCE

A very fine Inorganic Chemistry School was present at the University of Adelaide in the early 1960s. Bruce West, Tom Bell and Alan Jones were staff members with interests in organometallic chemistry. Graduates in inorganic chemistry from that era include Glen Deacon, Ron Dickson, Max O'Connor, Bob Cattrall and Brian Pullman. Tom Bell and Alan Jones left Adelaide for Simon Fraser University and the Univesity of Norwich, respectively.

Bruce West graduated from the University of Adelaide with a First Class B.Sc. (Hons.) degree in 1949, became a Commonwealth Reconstruction Training Scheme Lecturer in 1949, and a Lecturer in Inorganic Chemistry in 1950. The Commonwealth Reconstruction Training Scheme was an Australian Government programme under which additional staff were appointed to Universities in the late 1940s to aid in teaching the increased enrolments coming from returned servicemen underaking university study. Chemistry departments tended to get such appointments because of their large service teachng contribution (medicine, dentistry, engineering). West was appointed in his B.Sc. (Hons.) year because of a staff shortage. Before then, inorganic chemistry had been taught at the University of Adelaide by William Cooke, an analytical chemist, from about 1910 until 1948.

In 1954, West and the late Rolly Pettit were awarded the third and fourth Ph.D. from the University of Adelaide in any discipline. The first Ph.D. from the University of Adelaide was awarded in 1952 to Lloyd Jackman (now at Pennsylvania State University). Rolly Pettit's Ph.D. work was in organic chemistry, and was supervised by Professor G. M. Badger. Pettit went to University College, London, to work with Michael Dewar on the tropylium ion.[75–77] Tom

Mole was at that time a student of Dewar's, working on organic electrophilic substitution.[78,79] Interestingly, it was to be Pettit's later work on iron carbonyl complexes of neutral and ionic conjugated polyenes, which stimulated Arthur Birch's interest in the iron carbonyl cyclohexadiene system (see section entitled 'Nyholm and Birch').

West's Ph.D. work at Adelaide on metal exchange reactions was carried out without supervision. In order to gain the experience of directed research that he felt was needed to supervise others, West took leave to go to Cambridge at the beginning of 1953 to work as a Ph.D. student with Harry Emeléus. Emeléus was developing a school of fluorine chemistry in all of its aspects, and it was here that West developed an interest in organometallic chemistry. West examined the reaction between perfluoromethyl iodide (CF_3I) and Group 15 organometallics [$P(CH_3)_3$, $As(CH_3)_3$, etc.] in collaboration with Bob Haszeldine, then an Assistant Director of Research. This work cemented his life-long interest in organometallic chemistry, as well as providing an introduction to a 'synthetic' vacuum system, pressure vessels and glass-blowing—techniques taken back to Adelaide and used in research projects from 1956 onwards. The Cambridge work disclosed the ability of CF_3 groups to exchange with alkyl groups attached to phosphorus, arsenic or antimony and was published as 'Radical exchange in organometallic compounds'.[80,81]

Following completion of his Ph.D. at Cambridge in 1955, West returned to the University of Adelaide. He was able to attract a succession of outstanding Ph.D. students who worked on both organometallic and coordination chemistry problems. The first 'organometallic group' consisted of Brian Pullman, Ron Dickson and Glen Deacon.

Dickson commenced work on Ziegler–Natta-type catalyst systems, looking at alkali metal derivatives of Group 14 alkyls with $[Ti(cp)_2Cl_2]$, an area suggested by Professor D. O. Jordan, who was very interested in polymerization processes. This led to further work on $Li[AlEt_4]$ reactions with various halides.[82,83] Pullman completed the Group 15 series reactions with R_FI by looking at bismuth alkyls. This work was aided by the skills of T. N. Bell, a Lecturer in the Department of Inorganic and Physical Chemistry, who was expert in high-vacuum chemistry and the then new technique of gas chromatography.[84]

Tom Bell's assistance materially aided the synthesis of the first ditelluride perfluoroalkyl, $[(CF_3Te)_2]$ using CF_3 radical attack on tellurium mirrors, and $[Bi(CF_3)_3]$ was produced by a related procedure.[85]

Glen Deacon commenced work on aryl–Group 15 interactions with CF_3I, but this proved a rather difficult route to mixed aryl-perfluoroalkyls, and he moved to studies on mercury phosphine compounds and their interactions with alkyl halides.[86] Dickson subsequently went to work with Geoffrey Wilkinson and gained his interest in cyclopentadienyl–carbonyl chemistry, Deacon went to Ronald Nyholm and developed an interest in perfluoroaryl organometallics, while Pullman went to the Australian Mineral Development Laboratories and thence to ICI (Australia).

A chance conversation with Ted Walton (UNSW) while both were on leave at University College London in 1961 drew West's attention to the structure of 'arsenobenzene', and led to his interest in the polycyclophosphines and arsines of Group 15, initially as possible π-bonding ligands, then as unconventional complexing agents to metal carbonyls. He commenced some work on $[(C_6H_5As)_6]$ at University College, but it was not until Ang How Ghee joined him in Adelaide from Malaysia in 1962 that progress was made. The first authentic polyphosphine complex was reported, and its characterization was aided by mass spectral measurements by J. S. Shannon.[87,88] Ang accompanied West to Monash when West took up the Chair of Inorganic Chemistry in 1964 and helped in the extension of these studies to other Group 6 and 7 metals. Ang became the first 1851 Exhibitioner from Monash, and went to Cambridge to work for H. J. Emeléus. After holding a Research Fellowship at Peterhouse, Ang returned to Singapore where he is Professor of Chemistry at the University of Singapore. Ang has also served as Director of the Singapore DSIR.

West's student, Patricia Elmes, reacted polyarsine derivatives with Group 6, 7 and 8 metals.[89,90] She showed that long-chain (As_8, As_9) arsines could form by association of fragments during reaction[91] and that the elusive analogues of azobenzene, phosphoro- and arseno-benzene, could be trapped as $R_2As_2(P)$ molecules bound in bidentate fashion to metal π-complex residues.[92,93] Structural studies were performed in collaboration with West's Monash University colleague Brian Gatehouse and his students.

Ring sizes in cyclic perfluoroalkylphosphines have also been characterized by combined ^{19}F NMR and mass spectral studies.[94] Much of the work on polycyclic derivatives has been reviewed.[95] Patricia Elmes is now a senior research worker at Monash University in Professor R. D. Brown's galactochemistry group.

West and R. R. Schrieke attempted to use SiF_3I to develop a perfluorosilyl chemistry to compare with the extensive perfluoroalkyl field, but the reagent was not comparable with CF_3I in its wide applicability. However, a number of metal carbonyl derivatives were isolated.[96] Perfluoroarylsilyl derivatives were readily obtainable.[97] R. R. Schrieke is now Head of the Chemistry Department at the Ballarat Institute of Avanced Education. West's twin interests in organometallic and coordination chemistry were brought together by synthetic studies on organometallic compounds having the metal in relatively high oxidation states [M(II) or (III)] with other acid–base chelate ligands coordinated to the metal. The readily available salicylaldimine and dithiocarbamate ligands have proved excellent co-ligands in many of the studies. These have included the synthesis and often structural characterization of perfluoroalkyl cobalt(III)[98] and chromium(III)[99] derivatives, alkylrhodium(III),[100–102] alkyl, π-allyl, amine-chelated phenyl derivatives of platinum(II), palladium(II)[103–105] and dimethyl gold(III) compounds.[106] Physicochemical studies involving such molecules have included the discovery of alkyl group exchange by a redox reaction between R-Co(III) and Co(II) salicylaldimines or tetradentate β-ketoimines, which could be followed by ^{19}F NMR spectroscopy,[107,108] the electrochemical generation and study of the very unstable alkyl and perfluoroalkyl cobalt(II) salicylaldimine complexes,[109] and examination of the spectral properties of π-allyl molybdenum carbonyls.[110] Dr B. E. Reichert, who was involved in much of this work, held an ICI Research Fellowship at Cambridge and now works for ICI in Australia. Another collaborator, Adrian van den Bergen, is a senior research worker with West's group at Monash.

West's colleague Keith Murray, a coordination chemist, was associated with many parts of this work, particularly the early work involving cobalt and rhodium derivatives. The Burrows Lecture, delivered in 1981 on receipt of the Inorganic Chemistry award of the Royal Australian Chemical Institute at Queenstown, New Zealand, was concerned with this merging of the two streams of chemistry.[111] Research in coordination chemistry took precedence after 1980, apart from some excursions into the electrochemical synthesis of organometallics,[112] including acetylides.[113] However, in collaboration with Ron Dickson and Glen Deacon and other groups in the CSIRO Division of Materials Science and Technology and Telecom Research Laboratories, a programme of synthesis of special organometallics for use in MOCVD processes leading to semiconductor wafer preparation commenced in June 1988. Publications from this work are beginnng to appear.[114]

Following the move of Professor Don Stranks from the University of Adelaide to the University of Melbourne, **Michael Bruce** was appointed Professor of Inorganic Chemistry within the Department of Physical and Inorganic Chemistry of the University of Adelaide in 1973, and became Angas Professor of Chemistry after the retirement of Professor D. O. Jordan in 1982. Michael Bruce had been an Open Exhibitioner at Lincoln College, Oxford, from 1957 to 1961, and obtained his B.A. (Hons.) degree at Oxford in 1961. He then spent the years 1961–1964 in Australia working as an Experimental Officer in the Biochemistry Section of the CSRIO Division of Plant Industry in Canberra. Studies initiated there into natural and synthetic plant cell-division inducers (cytokins) led to the discovery of an extensive new class of synthetic materials of this type. His later interests in the applications of mass spectroscopic techniques to organometallic chemistry were stimulated by his collaborations with the mass spectroscopists in the Division of Plant Industry. Michael Bruce moved to Bristol in 1965, becoming a Junior Fellow from 1966–1967, and completed his Ph.D. under the supervision of Professor Gordon Stone at Bristol in 1967. From 1967 until his move to Adelaide in 1973, he was a Lecturer in Inorganic Chemistry at the University of Bristol. Michael Bruce is well known for his extensive contributions to *Annual Surveys of Organometallic Chemistry* since 1969, and to the Royal Society of Chemistry's *Specialist Periodical Reports on Organometallic Chemistry.* He has also contributed the sections on the mass spectrometry of inorganic and organometallic compounds in the *Specialist Periodical Reports on Mass Spectroscopy*, as well as an article on the subject in *Advances in Organometallic Chemistry.*[115] The latter series has also contained several of his accounts of the development of the literature of organometallic chemistry. Bruce is co-author (with Professor F. G. A. Stone) of the article on 'Organometallic compounds' in *Encyclopedia Britannica*, and contributed the section on 'Ruthenium' (with Martin Bennett and Trevor Matheson) and a unique Structural Index to *Comprehensive Organometallic Chemistry*. His review on cyclometalations is still widely quoted.[116] Michael Bruce's contributions to chemistry and organometallic chemistry have been recognized by the receipt of the RACI's 1986 H. G. Smith Medal and the RACI Inorganic Chemistry Division's 1989 Inorganic Chemistry Award, marked by his delivery of the G. J. Burrows Lecture at the XXVII ICCC in Queensland, his appointment as 1986 Royal Society of Chemistry Lecturer, Australia, and his election as a Fellow of the Australian Academy of Science in 1989.

Michael Bruce's group at Adelaide has made important and extensive contributions to organometallic chemistry in several areas. These include cyclopentadienyl ruthenium and osmium chemistry, and the development of the novel ligand $[C_5(CO_2Me)_5]^-$, metal cluster chemistry, the reactivity of vinylidene ligands in various bonding modes, the organometallic chemistry of gold, including the development of the reagent $[Au(PPh_3)_3O][BF_4]$ as a source of $AuPPh_3$ fragments isolobal with the proton, and the application of FAB MS to the analysis of inorganic and organometallic compounds.

Bruce's work in cluster chemistry has concentrated on the chemistry of polynuclear ruthenium complexes. The development of radical ion-initiated routes to the substitution of metal carbonyl cluster compounds under mild conditions has been of particular interest.[117–121] A wide range of simple ligand-substituted derivatives, and mixed ligand complexes, e.g., $M_3(CO)_{12-n}L_n$ ($M = Ru$, Os, $n = 1$–4), as well as reactive complexes such as olefin–Ru_3 clusters have been prepared, and their structural chemistry studied systematically.[122–128] The synthesis of a bis-tertiary phosphine cluster containing two Ru_3 clusters linked by a $P—P{\equiv}C—P$ system was achieved in this fashion. This di-cluster condenses to a higher-nuclearity cluster containing an open Ru_5 cluster on gentle heating. The reactivity of the C_2 unit in this cluster is enhanced by its interaction with the cluster, and many of its unusual reactions provide further insight into the behaviour of small molecules on metal surfaces.[129–133]

Prior to this work, CO substitution in iron, ruthenium and osmium clusters required such forcing conditions that subsequent cluster fragmentation or ligand transformation reactions occurred, the substitutions were non-selective, and, in general, only thermodynamically and kinetically stable derivatives were accessible. The mild Me_3NO-induced substitution of osmium clusters does not work for the iron and ruthenium systems.

The application of $[O\{Au(PPh_3)_3\}]^+$ to the synthesis of heterometallic clusters containing gold provided a new route to these complexes, which have novel cluster geometries, and model the interaction of H_2 and H_3^+ with metals.[134–137]

Bruce has also contributed significantly to the study of reactions of transition metal complexes containing M–C(*sp*) or M–C(sp^2) bonds.[138] Synthetic routes such as electrophilic addition to metal acetylides, and the metal-induced isomerization of 1-alkynes, have led to a wide range of vinylidene complexes, and, in turn, their derivatives.[139–144] The susceptibility of the β-carbon of metal acetylides towards addition was further exemplified by the cycloaddition of electron-deficient olefins to give a series of cyclobutenyl, butadienyl and allylic compounds with unusual properties. Much of this work utilized the ability of the $[M(PR_3)_2(\eta^5\text{-}C_5H_5)]$ ($M = Ru$, Os; $R = Me$, Ph, etc.) fragment to stabilize unusual ligands.[145–148]

More recently, the strong organic acid $HC_5(CO_2Me)_5$ has been shown to form metal derivatives with a range of bonding modes, ranging from η^5, through 'slipped' η^3 *C*-bonded, to chelating *O*-bonded and purely ionic. These complexes have a range of unusual properties, including water solubility.[149–153]

MONASH UNIVERSITY

In accepting the Foundation Chair of Inorgnic Chemistry at Monash University in 1964, Bruce West (see above) recognized that organometallic chemistry was under-represented in Australia at that time, and that a fine group of organometallic chemists (Mole, Wailes, etc.) was located at the nearby CSIRO Laboratories in Melbourne. He decided to establish Monash University as a centre of organometallic chemistry in Australia in the 1960s. Monash therefore recruited **Ron Dickson**, **Glen Deacon** and, later, **Roy Jackson**.

Ron Dickson obtained his B.Sc. (Hons.) (1958) and Ph.D. (1963) degrees at the University of Adelaide under the supervision of Bruce West, working chiefly on organometallic chemistry, predominantly of organoaluminium compounds, related to Ziegler–Natta catalysis.[82,83] During an appointment as a CSIRO Postdoctoral Fellow, working with Professor Geoffrey Wilkinson at Imperial College, Dickson was attracted to fluorocarbon–rhodium complexes and the general area of alkyne–transition metal chemistry which has remained his major research interest.[154,155] While at the University of British Columbia as an Instructor in 1963/1964, Dickson prepared the first stable fluorocarbon–aluminium compounds.[156] He joined the academic staff of the then-fledgling Department of Chemistry at Monash University in 1964 as a Lecturer. Investigations of the products formed from reactions between alkynes and carbonyl–cobalt compounds dominated those early years. The use of electron-withdrawing trifluoromethyl substituents to stabilize Co–C bonds in flyover bridge complexes was a major achievement.[157,158] Dickson's 1974 review on alkyne–cobalt carbonyl chemistry is still the definitive work in this area.[159] Ron Dickson's interests moved naturally to carbonyl complexes of the congener elements rhodium and iridium,[160] and the last decade has been dominated by studies of dinuclear and polynuclear complexes, particularly those of rhodium. Multinuclear, temperature-variable and lanthanide-shifted NMR spectroscopic techniques were developed to follow the dynamic processes of many of the complexes in solution, and to unravel the unexpected geometrics or unusual modes of coordination of many of the ligand systems.[161]

During these studies, the complexes $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO_2)(CF_3C_2CF_3)]$ and $[(\eta^5\text{-}C_5H_5)_2\text{-}Rh_2\text{-}(CO)(CF_3C_2CF_3)]$ were discovered.[162,164] The remarkable alkyne rotation that accompanies the facile conversion of one of these compounds to the other aroused considerable interest.[165,166] The monocarbonyl compound proved to be an extraordinarily versatile reagent for studying many of the reactions which are important in homogeneous catalysis, particularly insertion, and coordinative and oxidative addition reactions.[167] Moreover, the retention of a metal–metal bond during these reactions added greater versatility to the reaction types that could be studied. Novel sunlight-promoted C–H bond activation reactions were achieved under extremely mild conditions with alkenes, polyenes, arenes and heterocyclic compounds.[168] The related N–H bond activation was also observed with amines. A host of interesting C–C, C–O and C–N forming reactions were observed in the reactions with alkynes, isocyanides, isocyanates, carbenes, nitrenes, heterocumulenes and other substrates.[169–171]

In collaboration with Brian Robinson and Jim Simpson, and with Alan Bond, Dickson's group has also demonstrated an increased lability of the coordinated ligands, following electrochemical oxidation or reduction of these di- and polynuclear metal complexes.[172,173]

Ron Dickson's recent work has involved the study of volatile organometallics for chemical vapour depositions of mercury cadmium telluride and doped semiconductors, and the formation and reactions of alkyne cluster compounds. Complexes in which one or more alkynes are linked to such polynuclear metal centres as Rh_3, Rh_2Co, Rh_2Ir, Rh_2Mn, Rh_4, Co_2Rh_2 and Rh_4Pt have been described.

Ron Dickson has also written two widely acclaimed texts devoted to the organometallic and catalytic chemistry of rhodium and iridium.[174,175]

Glen Deacon obtained his B.Sc. (Hons.) (1957) and Ph.D. (1962) degrees from the University of Adelaide under the supervision of Bruce West. Although his research was mainly in mercury coordination chemistry, studies with tertiary phosphines and arsines provided an introduction to organometallic chemistry. This was reinforced by a postdoctoral year at Adelaide in collaboration with Alan Jones working on the infrared spectroscopy of phosphonium compounds. Organometallic interests blossomed during a CSIRO Overseas Scholarship and an ICI Fellowship at University College London with Sir Ronald Nyholm, when Deacon prepared and studied the coordination chemistry of the first fluorocarbon–thallium compounds. In additional collaborations, Deacon developed decarboxylation reactions for the synthesis of fluorocarbon–mercurials with Alwyn Davies (University College London) and John Connett (National Chemical Laboratory, Teddington), and investigated the infrared spectra of a wide range of organometallics with John Green (NCL and NPL, Teddington).

After appointment to a lectureship at Monash University in 1966, Deacon initially concentrated on Main-Group element organometallic chemistry, and this has continued to be a strong research interest. He has become well known for his investigations on organic derivatives of mercury and thallium, especially perfluorohalogeno compounds, a field in which he was the pioneer. These studies were extended to perhalogeno organometallics of a wide range of elements, notably bismuth, indium, tin and germanium. This work developed the decarboxylation of metal carboxylates as a very effective route to the synthesis of organometallics, especially the perfluoro- and perchloroaryls. Areas explored have included the effect of polyhalogenoaryl ligands on organometallic coordination chemistry, the synthesis of organometallics by elimination reactions (CO_2, SO_2, and the unprecedented SO_3),[176-178] sulphinate complexes of organometallics including the first linkage isomers of a sulphinate ion,[179-180] mercuration and thallation of highly deactivated polyfluoro- and polychloro-arenes, and development of new powerful metallation reagents, $[Hg(O_3SCF_3)_2]$, $[Tl(O_3SCF_3)_3]$, and $[Tl(O_2CCF_3)_3]/SbF_5/FSO_3H$.[181] Structures of organomercurials and definition of weak coordination interactions have been a continuing interest,[182] as has been the use of permercurated arenes[183-186] and unusual mercuration patterns in organic synthesis,[187] and the biological role of mercurials. Recent studies have involved unexpected syntheses of polymethoxyphenylmercurials by decarboxylation,[188] studies of factors affecting competition between mercuration and decarboxylation, synthesis of oxygen-functionalized methylmercurials, and the use of aminomercuration to give difunctionalized primary aromatic amines, $RN(CH_2CH_2HgX)_2$.[189] A recent collaboration with Ron Dickson and Bruce West has extended Deacon's Main-Group organometallic interests to precursors for production of $Hg_xCd_{1-x}Te$ by MOCVD. Deacon was awarded the D.Sc. degree of the University of Adelaide in 1972 for studies in Main-Group element chemistry, and was appointed Reader in Chemistry at Monash University in 1975.

Following study-leave as an Honorary Research Associate at University College London in 1972, Deacon began work in what is now his main research interest, rare-earth organometallics. He performed seminal work in the synthesis and characterization of organometallic compounds of ytterbium(II), the first fluorocarbon organolanthanoids and in the development of general synthetic routes to cyclopentadienyl derivatives of lanthanide elements in the oxidation states +2 and +3. The preparation of cyclopentadienyl-lanthanide derivatives by redox transmetallation reactions is now used routinely by workers in this field. The very restrictive synthetic methods available for these highly air- and water-sensitive organometallics posed a major synthetic challenge. Redox transmetallation reactions of lanthanoid metals with mercurials[190] and thallium cyclopentadienides,[191,192] and displacement of weaker carbon acids by stronger ones were developed for the synthesis of organolanthanoids. The ready availability of $[cp_2Yb]$ by redox transmetallation[191,192] has facilitated the investigation of its oxidation reactions giving $[cp_2YbX]$ compounds (e.g. 193, 194) and the study of its coordination chemistry.[195] New reactions of organolanthanoids have particularly involved the fluorocarbon–lanthanoids, $[(C_6F_5)_2Ln]$ (Ln = Yb, Eu or Sm—the last only available by trapping) in protolytic ligand exchange with C–H, N–H, and C–O–H acids[196,197] and organic synthesis, e.g., reduction, arylation, and selective dehalogenation.[198] Redox transmetallation and ligand exchange reactions have been combined to give cyclopentadienyl-, aryloxo-, and organoamido-lanthanoids[196] in 'one-pot' syntheses. Low-coordination lanthanoid(II) and (III) complexes of the last two classes, stabilized by bulky ligands,[196,197] have been isolated. Recently, the phosphinoytterbocene, $[Yb(C_5H_4PPh_2)_2]$, has been prepared by ligand exchange from $[(C_6F_5)_2Yb]$ and by redox transmetallation, and converted into *f*-block heterobimetallics.[199] As a consequence of his studies into cyclopentadienylcerium complexes, Deacon was also able to establish that a large number of organocerium compounds, previously thought to be organocerium(IV) compounds, were in fact cerium(III) derivatives. Many of these investigations were carried out at a time when the chemistry of the rare earths was very neglected, under-developed and unfashionable.

Beginning in the late 1970s, Deacon's interests expanded to include reactions of ruthenium carbonyls, particularly for the synthesis of complexes with heterocyclic nitrogen donors,[200] and to decarboxylation and desulphination syntheses of precious metal organometallics (Ni, Pt, Pd, Rh, Ir) with fluorocarbon ligands.[201,202] Recently, synthetic routes to $[PtR_2(diene)]$ and $[PtR(Cl)(diene)]$ (R = poly-fluoro-phenyl) complexes were developed, and their diene displacement reactions studied.[203,204] An exciting development has been the synthesis of novel, water-stable, fluorocarbon-stabilized platinum organoamides, e.g. $[Pt(NRCH_2)_2L_2]$ and $[Pt(NRCH_2CH_2NMe_2)L(X)]$ (R = poly-fluoro-phenyl) from decarboxylation reactions originally intended to give organometallics,[205] and the discovery that these complexes have anticancer activity.

In 1984 and 1988, Deacon held Guest Professorships at Dortmund University and the Technical University, Berlin. His work has involved many collaborations, particularly those with Jack Miller (Brock University, Canada) in mass spectrometry, Bryan Gatehouse, Gary Fallon and Peter Mackinnon (Monash University), Mary McPartlin (Northern Polytechnic), Allan White (University of Western Australia) and Edward Tiekink (University of Adelaide) with X-ray crystallography, and David Black (Monash University and University of New South Wales) with organic synthesis.

Roy Jackson accepted the Chair of Organic Chemistry at Monash University in 1973. Jackson, a B.Sc. graduate of the University of Manchester in 1955, completed his Ph.D. in 1958 at King's College, London. He worked with H. B. Henbest on organic stereomechanistic chemistry. His interest in organometallic chemistry began in 1958 when he was appointed US Ethyl Corporation Postdoctoral Fellow in the Dyson–Perrins Laboratory in Oxford under the supervision of Sir Ewart Jones and Mark Whiting. Mark Whiting and Barry Nicholls had just discovered how to make tricarbonyl(arene) complexes of chromium, molybdenum and tungsten from the appropriate metal carbonyl (donated by Ethyl Corporation). E. O. Fischer and Fausto Calderazzo and their co-workers had made similar discoveries quite independently in the same year. Jackson, an organic chemist, became interested in how the presence of the tricarbonylmetal group affected the reactivity of the arene ligand. He moved to Queen's University, Belfast in 1959 as a lecturer and extended this interest to a range of reactions. One example arose from a ^1H NMR study of these compounds (NMR spectrometers had just become available) which showed that the tricarbonylchromium group had a preferred staggered arrangement in $[(\text{t-butylbenzene})Cr(CO)_3]$ (for steric reasons) but a preferred eclipsed conformation in $[(\text{toluene})Cr(CO)_3]$ (for electronic reasons.[206] Jackson recognized that this conformational preference could lead to highly unusual regioselectivities in the attack of bulky electrophilic reagents, and thus showed that Friedel–Crafts acylation of $[(\text{t-butylbenzene})Cr(CO)_3]$ gave acetyl compounds in the *meta*:*para* ratio 87:13, in contrast to the reaction of t-butylbenzene under similar conditions which gave a *meta*:*para* ratio of 4:96.[207]

A visit to Monash by Martin Semmelhack led to further development of the concept of regioselectivity based on conformational preferences in the metalarenetricarbonyls. Jackson and Semmelhack jointly showed that the conformational concept could be used to explain the regiochemistry of nucleophilic as well as electrophilic reactions.[208]

Another aspect of ligand reactivity which Jackson examined in collaboration with colleagues in Belfast involved attempts to correlate the reactivity of ligands coordinated to metals in discrete complexes with reactions of the same ligands over heterogeneous metal catalysts. Hydrogenation and hydrogenolysis reactions were of particular interest.[209]

Jackson extended and continued his studies of modified ligand reactivity in collaboration with collegues at Monash after his arrival in Australia in 1973. Attention was focused on reactions which led to the synthesis of compounds of significant theoretical or biological interest. David Collins and Jackson used π-allylpalladium compounds to prepare 6β-acetic acid derivatives of steroids and steroidal hormones such as progesterone and testosterone with both regio- and stereo-specificity. The pseudo-axial 6β-compounds were readily equilibrated to the more stable, pseudo-equatorial 6α-compounds.[210,211]

Jackson presented this work at one of the Oxford–Cambridge Synthesis meetings in the late 1970s and was horrified by a remark of Gilbert Stork that although the work was interesting, nobody would really be interested unless the reactions could be made catalytic in palladium. Jackson took this comment to heart and decided to concentrate on catalytic reactions on his return to Australia.

At this time, interest in catalytic enantioselective synthesis was rapidly developing. The major emphasis was on asymmetric hydrogenation reactions and, to be different, Jackson concentrated on enantioselective carbon–carbon bond-forming reactions. The initial choice of reaction was the palladium-catalysed addition of hydrogen cyanide to alkenes which gave alkyl cyanides in modest enantiomeric excess (e.e. <30%).[212] It became obvious to Jackson that in order to achieve better e.e. values it was important to understand the factors which led to overall regio- and stereo-control of metal-catalysed reactions and also that new chiral ligands were required. Evaluation of the existing literature data suggested that 1,4-diphosphines in which one phosphorus atom was directly linked to a chiral carbon atom would be ideal for enantioselective hydrocyanation and hydroformylation reactions. Steroid-based diphosphines were prepared in efficient syntheses. Alas, although the ligands proved to be useful in enantioselective hydrogenation reactions, they gave disappointing results in hydroformylation and hydrocyanation reactions.[213]

Jackson then concentrated on the use of steric effects, electronic effects and chelation of the metal to a remote substituent to achieve good regio- and stereo-control of organic reactions involving organometallic catalysts. Several syntheses of novel compounds and new, efficient syntheses of biologically important classes of compounds have been achieved.

Jackson's utilization of steric effects is exemplified by the incorporation of a large group on one end of a double or triple bond. This leads to preferential metal–carbon bond formation at the end remote from the bulky group. The use of bulky silyl groups (e.g. t-butyldiphenylsilyl or triphenylsilyl) was particularly effective and the silyl group could be further manipulated in the products. The reactions chosen for study were the nickel-catalysed hydrocyanation of alkynes[214] and the ruthenium-catalysed hydroformylation of alkenes.

The hydrocyanation route was used to synthesize the biologically important α-methylene-γ-lactones,[215,216] the novel α-methyl-β-lactone,[217] new γ- and δ-amino-acids, and unsaturated amino-acids, such as one found in Hawaiian sponges.[218] Catalytic hydroformylation was applied to a new synthesis of aldols.[219,220]

More recently, Jackson has shown that the electronic effects of the tricarbonylchromium group can be used to achieve regio-control in reactions of arene substituents. Thus, the hydroformylation of styrenes normally gives a preference for the branched-chain aldehyde. However, Jackson demonstrated that these reactions can be made regiospecific by using the tricarbonylchromium derivatives of the styrenes.[221] The tricarbonylchromium group can easily be removed by mild oxidation.

Jackson has also achieved complete regio- and stereo-control of metal-catalysed reactions by using potentially chelating substrates with ligating substituents γ to the organic functionality. Examples include the rhodium-catalysed hydroformylation of alkenylphosphines,[222,223] and alkenylphosphites.[224]

More recent work has focused on substituents which can interact with either the transition state or the product, thus leading to new heterocyclic synthesis. Novel syntheses of nitrogen heterocycles including pyrroles, piperidones, and medium-ring heterocycles have been developed.[225]

Over the past ten years. Jackson's studies in catalytic asymmetric synthesis have been carried out in collaboration with ICI Australia Pty Ltd. The targets have been molecules of commercial interest to the company in the area of agrochemicals and pharmaceuticals. In the latter area a synthesis of the cardiac drug (+)-Diltiazem has recently been completed.[226] The synthesis involved the development of a catalytic version of the asymmetric osmium-catalysed dihydroxylation of alkenes originally developed by K. B. Sharpless.

Allan Canty completed a Ph.D. at Monash University in 1971, working in the area of organomercury chemistry and crystallography with Glen Deacon and Bryan Gatehouse. He was one of the first Ph.D. students supervised by Glen Deacon after Deacon's arival at Monash University, and began by investigating the synthesis and characterization of phenyl and pentafluorophenyl complexes of mercury. Following a period of two years with Jack Lewis at Cambridge, Canty returned to a lectureship at the University of Tasmania, where he is now a Reader. His work in Tasmania had been concentrated on the biological chemistry of mercury,[227–230] the coordination chemistry of organometal cations of mercury,[231,232] gold,[233] thallium[234] and indium,[235] and more recently on the organometallic chemistry of platinum and palladium.[236–242] A central theme of the work has been the synthesis and application of flexible polydentate nitrogen donor ligands in the organometallic chemistry of methylmetal species.[231–240] Notable achievements include the synthesis at Cambridge of the ruthenium ethylidyne complex $[H_3Ru_3(CO)_9CMe]$ with Jack Lewis,[243] the development of high-coordination geometries for $MeHg^+$,[231,232] a widely quoted comment on the van der Waals radius of mercury,[244] unusual cyclometallation and intramolecular coordination systems for palladium and platinum,[236,237] the development of synthetic routes to alkylpalladium(II) chemistry,[238] and the discovery of oxidation state +IV alkylpalladium chemistry in 1986.[239–242] Canty is part of the link back to Emeléus and Cambridge, and his work in Tasmania has benefited from stimulating sabbatical leave periods with R. Stuart Tobias,[229] Arthur J. Carty (a collaboration which can cause some confusion in the literature),[230] and Richard J. Puddephatt,[242] and very generous crystallographic contributions to his work by Bryan Gatehouse[231] and Allan White.[232–237,240,241]

CSIRO IN MELBOURNE

The discovery of Ziegler–Natta olefin polymerization catalysts inspired an enormous amount of organometallic chemical investigation worldwide. Much, but not all, of this effort in Australia was concentrated in the laboratories of the Commonwealth Scientific and Industrial Research Organization's (CSIRO) Divisions of Organic Chemistry, of Mineral Chemistry and of Physical Chemistry in Melbourne. The then Chiefs of these Divisions were Dr Jerry R. (now Sir Robert) Price, Dr Ivan Newnham and Dr Keith Sutherland (followed as Chief of the Division of Physical Chemistry by Dr Sefton Haymann), respectively, and the staff working on organometallic chemistry included Peter Wailes, Tom Mole, Bob Coutts, Alan Reid, Malcolm Winfield and John Swan.

John Swan had been working on the chemistry of wool at the CSIRO Division of Protein Chemistry in the 1960s, when Jerry Price persuaded him to join the Division of Organic Chemistry. Price was the inaugural Chief of the Division of Organic Chemistry, later the Division of Applied Chemistry, and now the Division of Chemicals and Polymers. On his arrival at the Division of Organic Chemistry, Swan initiated a programme of research on 'Metals of economic importance to Australia'. Swan worked on phosphorus chemistry, and later moved into academia, eventually becoming a Pro Vice-Chancellor at Monash University. **Tom Mole** and co-workers studied the chemistry of aluminium, the late **Charlie Kowala** investigated organogold compounds,[245–248] and **Peter Wailes** and co-workers worked on the chemistry of titanium and zirconium. Much of this work was based on cyclopentadienyl compounds and involved very fruitful collaborations with **Alan Reid**, **R. S. (Bob) Coutts**, and **Helmut Weigold**.

Peter Wailes obtained his B.Sc. (Hons.) and M.Sc. degrees in organic chemistry at the University of Sydney, under the supervision of Dr Stephen Angyal and Dr P. Cymerman-Craig, respectively. He obtained a CSIRO Postgraduate Fellowship and went to the University of Manchester in 1952, where he obtained his Ph.D. under the supervision of Professor E. R. H. Jones. Wailes' Ph.D. work involved investigations of the reactions of acetylenes with metal carbonyls,[249,250] and had been stimulated by the Second World War work of Walter Reppe in Germany. In 1954, Wailes took up a position as Research Scientist within the Organic Chemistry Section of the CSIRO Industrial Chemistry Laboratories in Melbourne. His original work there involved the utilization of tallow, and the development of a variety of organic insecticides. However, following the move of John Swan to what was by then the Division of Organic Chemistry, Wailes began the work on titanium and zirconium cyclopentadienyl chemistry for which he has become well known. Wailes collaborated with Alan Reid (a New Zealander, now Director of the CSIRO Institute of Minerals and Engineering), a very talented synthetic inorganic chemist in the Division of Mineral Chemistry, in the development of new preparations of cyclopentadienyl compounds using vacuum-line techniques.[251,252] They synthesized [$Mncp_2$], and developed several syntheses of the useful reagent, [$Mgcp_2$],[253] one of which involved bubbling cyclopentadiene through a molten lead/magnesium alloy. This process was patented and taken to the pilot-plant stage.[254] A considerable body of work was devoted to the synthesis and study of titanium(III) cyclopentadienyl derivatives. Wailes, Coutts and Weigold produced what was for many years the definitive work in this area.[255] (The recent treatise, *The Organometallic Chemistry of Zirconium and Hafnium*, was co-authored by Professor Colin Raston of Griffith University, Queensland.) Several collaborative projects were established with Bruce West, when West moved to Melbourne as Professor of the newly established Monash University in 1964. Wailes is currently a Chief Research Scientist, and Assistant Chief of the CSIRO Division of Chemicals and Polymers.

Bob Coutts joined CSIRO in 1964 after obtaining Diplomas in Metallurgy and in Applied Chemistry from the Ballarat School of Mines and Industries. He then completed a conversion course to M.Sc. under the supervision of John Kingston at the new La Trobe University in 1969. At that time Professor Ray Martin, then at the University of Melbourne, was interested in studying the spin–spin interaction of dimers of the bis(cyclopentadienyl)titanium(III) halides (the fluoride was unknown and the iodide had not been characterized).[256,257] Coutts gained his Ph.D. in 1972 from the University of Melbourne under the supervision of Professor Ray Martin, and the co-supervision of Peter Wailes, working on the bis(cyclopentadienyl)titanium(III) halide dimers and on the chemistry of the monocyclopentadienyltitanium(III) moiety.[258–260] An interest in organometallic coupling agents, and his earlier training in metallurgy, resulted in Coutts transferring to the newly formed CSIRO Division of Chemical Technology in 1974 to study fibre composite materials.[261] Bob Coutts is now a Senior Principal Research Scientist at the CSIRO Division of Forestry and Forest Products and one of his interests is the surface treatment of wood and wood fibres using organometallic reagents.

Helmut Weigold was born in Palestine of German parents. The family was among German nationals shipped out to Australia and interned near Tatura, Victoria, during the Second World War. Weigold obtained his Ph.D. from the University of Adelaide under the supervision of Bruce West and, after postdoctoral work with Jack Lewis in Manchester and John Fackler in Cleveland, joined the CSIRO Division of Applied Chemistry. Much of his early work in collaboration with Peter Wailes involved the preparation of a new series of zirconium hydrides.[262–267] They reacted cp_2ZrCl_2 with $LiAlH_4$ to produce $cp_2Zr(H)Cl$,[262,263,265,266] now known as Schwartz's reagent,[268] and first reported the reactions of $cp_2Zr(H)Cl$ with carboxylic acids, olefins and alkynes. Weigold is now with the CSIRO Division of Chemicals and Polymers and is currently investigating organometallic antiviral agents in collaboration with George Holan.

The formation of hydrogenation catalysts from aqueous solutions of cobaltous chloride and excess potassium cyanide[269] was studied extensively at the CSIRO Division of Physical Chemistry in Melbourne in the 1950s and early 1960s, by **Malcolm E. Winfield** and his collaborators, J. H. Bayston and N. Kelso King.[270–278] Winfield spectrophotometrically examined these solutions and their interactions with hydrogen,

$$2\,[Co(CN)_5]^{3-} + H_2 \rightleftharpoons 2\,[Co(CN)_5H]^{3-}$$

and identified the $[Co(CN)_5]^{3-}$ (later prepared as its tetra-alkyl-ammonium salts[279,280] and $[Co(CN)_5H]^{3-}$ ions. The presence of the hydride had previously been established by Griffith and Wilkinson[281] by ^1H NMR. Winfield also examined the interactions of oxygen with $[Co(CN)_5]^{3-}$ to give $[(CN)_5Co(\mu\text{-}O_2)Co(CN)_5]^{6-}$ by ESR, and later moved on to the study of cobalt in biological systems (cobalamin, ribonucleotide reductase), as well as examining cytochrome *c*, by ESR, and studying the uptake of O_2 by iron porphyrins.[282–287] His earlier research interests had been in surface chemistry, and heterogeneous catalysis. Mal Winfield lives in retirement on a farm near the Victorian rural port of Lake's Entrance.

Tom Mole was born in England, and obtained his Ph.D. in organic chemistry under the supervision of Michael Dewar at the University of London. Following postdoctoral work with Bill Doering at Yale,[288] he took up an appointment at the CSIRO Division of Organic Chemistry in the early 1960s. In an extensive series of papers, Mole and his co-workers, who included **Norman Ham**, **John Saunders**, **John Surtees**, **E. A. (Ted) Jeffery**, **Aivers Meisters** and **Laurence Bagnell**, investigated the chemistry of organoaluminium compounds, which act as olefin oligomerization catalysts, or as co-catalysts in Ziegler–Natta polymerization systems. These investigations began with the development of reliable syntheses of $(C_6H_5)_{3-x}AlCl_x$ $(x = 0\text{–}2)$, and involved the formation of alkylaluminiums, alkylaluminium halides and hydrides;[289–291] and their interactions with Lewis bases.[292,293] Their classic work on the kinetics and mechanism of intra- and inter-molecular alkyl group exchange[294–300] included some early applications of the use of NMR in the study of organometallic exchange reactions.[301–303] They also studied bridging-phenyl, -phenylethynyl and -octynyl groups,[291,298,304–309] the preparation of some alkynyl derivatives of iron and molybdenum in collaboration with M. L. H. Green;[310] the chemistry of aluminium alcoholates, and of zinc, cadmium and mercury alkyls;[311–316] hydrogen isotope exchange on organic compounds, catalysed by alkylaluminiums;[317–320] reactions of $(alkyl)_3Al$ with benzanilides, ketones, aldehydes, α-picoline, alcohols and carboxylic acids; [321–329] and the nickel-catalysed reactions of Me_3Al with ketones, nitriles, α,β-unsaturated ketones and steroids.[330–337] The work is the subject of several reviews[299, 303] and patents[336, 337] and culminated in the test *Organoaluminium Compounds* by Mole and Jeffery, which is still an authoritative work on the subject,[338] and was the first systematic description of organoaluminium chemistry since the growth of interest in the field. Mole and Meisters developed some remarkable chemistry using trimethylaluminium, including converting carboxylic acids to t-butyl compounds (e.g. benzoic acid to t-butylbenzene).[328]

Tom Mole moved to the then CSIRO Division of Tribophysics (later the Division of Materials Science, and now the Division of Materials Science and Technology) where his investigations into the chemistry and catalytic applications of zeolites, particularly ZSM-5, have been equally productive and influential.

He also collaborated with **Jack Garnett** and **Merv Long**, both of the University of New South Wales, on the use of organoaluminium dihalides as catalysts for the deuteration and tritiation of organic compounds.[317–319] At that time, Garnett and Long were investigating an early example of catalytic organometallic C–H activation—the homogeneously catalysed H–D exchange of D_2O with aromatics by $[PtCl_4]^{2-}$ and $[H_2PtCl_6]$, and were comparing these catalysts with heterogeneous platinum catalysts.[339–343] The exchange was shown to occur in both the aromatic ring, and in the normally unreactive side-chains of alkylbenzenes.[344,345] Both $[RhCl_3]$ and $[Na_3IrCl_6]$ in CH_3COOD/D_2O were also precursors of homogeneous catalysts for the H–D exchange of alkylbenzenes and of cyclohexane at 130°C.[346–348]

The CSIRO work in organometallic chemistry, despite its obvious quality, was replaced by a combination of a perception that the Organization needed to be seen to be more 'applied', and the advent of the 1973 oil crisis. Many of the scientists involved with organometallic chemistry at that time became part of an inter-Divisional programme investigating the flash pyrolysis of coal.

THE UNIVERSITY OF MELBOURNE

Ray Colton's Ph.D. (1960) project involved the study of inorganic complexes of technetium and rhenium under the supervision of Professor (later Sir) Geoffrey Wilkinson at Imperial College, London. Martin Bennett (now at the Research School of Chemistry, ANU) completed his Ph.D., also under Wilkinson's supervision, at that time. Colton was next a Research Fellow at Harwell from 1960 to 1963. He was appointed as a Lecturer in Inorganic Chemistry at the University of Melbourne in 1963 and began an extensive investigation into carbonyl halide complexes of Groups VI, VII and VIII at the University of Melbourne in 1966. The work commenced with the synthesis of $Mo(CO)_4Cl_2$, the first neutral molybdenum carbonyl halide.[349] This compound was isolated during attempts to prepare $MoCl_6$ in high purity, by reacting pure molybdenbum metal, produced by pyrolysis of $Mo(CO)_6$, with Cl_2. Further work involved the syntheses and characterization of simple carbonyl halides and anions, of their complexes with dithiocarbamate, bis(diphenylphosphino)-methane and -ethane, and bis(diphenylarsino)methane ligands, and led to the development of an extensive chemistry of seven-coordinate molybdenum(II) and tungsten(II). One of these derivatives, $[Mo(CO)_2Cl_2py_2]$, is a remarkable 16-electron species with two unpaired electrons.[350] These studies also led to the preparation of the first 'A-frame' palladium(I) complexes with bis(diphenylphosphino)methane and bis(diphenylarisino)methane ligands—a field which many others have fruitfully followed.[351] In 1972, Colton and his Ph.D. student, Chris Commons, reported the earliest example of a complex with a four-electron bridging carbonyl ligand.[352] Colton and **Alan Bond** were among the first to examine the oxidative electrochemistry of a range of carbonyl complexes, and investigated the chemistry of the resultant paramagnetic organometallic compounds.[353]

Allan Casey was also on the staff at the University of Melbourne during this period. Casey had completed an Honours degree in 1950 at the University of Manitoba, and an M.Sc. in 1953 at the University of British Columbia, before gaining his Ph.D. in Cambridge in 1958. He joined the staff of the University of Melbourne as a Senior Demonstrator in 1958, and became a Lecturer in 1960. His research at the University of Melbourne has been primarily concerned with coordination chemistry, particularly of vanadium.[354,355] Coordination and organometallic chemistry were combined in the early 1970s, when Casey and a Ph.D. student, John Thackeray, examined a series of cp_2V^{IV} complexes with a variety of sulphur- and oxygen-donor ligands.[356,357] More recently, electrochemical syntheses of organometallic species using sacrificial electrodes have been described.[358,359]

No history of Australian chemistry would be complete without mention of the contributions of **Allan White**. A product of the School of Chemistry, University of Melbourne, Allan White obtained his Ph.D. in 1967. Since his move to the University of Western Australia, his X-ray crystallographic group has been extraordinarily productive, with over 500 publications appearing in the ten years to 1988. This work has embodied important, original and diverse contributions to chemical bonding, synthesis and properties of materials, as well as to systematic structural chemistry. These crystallographic investigations have encompassed all areas of chemistry, but the bulk of White's research has been in coordination and organometallic chemistry. Recent investigations have focused upon the structural chemistry of copper, silver and gold.

John Cotton obtained his M.Sc. under the supervision of Peter Fensham at the University of Melbourne in 1962. Fensham later moved to Monash University as Professor of Education. Cotton followed the not-uncommon practice of Australian graduates of that era, and travelled to England where he gained his Ph.D. at Cambridge in 1964 for work on non-aqueous solvents under the supervision of the late Tom Waddington. He was introduced to organometallic chemistry during postdoctoral work with H. C. Clark at Vancouver, and cemented this interest working with Professor Gordon Stone at Bristol between 1965 and 1967. In 1967, John Cotton took up a position at the University of Queensland, where he has pursued his research interests on mechanistic studies on the properties of metal–carbon bonds, particularly those in the carbonyl anions of iron, molybdenum and manganese. In 1973/1974 he spent a period of study-leave at the University of Sussex, collaborating with Professor Michael Lappert.

THE UNIVERSITY OF QUEENSLAND

Peter R. Wells (B.Sc. 1955) obtained his Ph.D. as an organic chemist in 1958, working on electrophilic substitution reactions of naphthalenes at the Leicester College of Technology and Commerce (now the Leicester Polytechnic) as an external candidate of the University of London, under the supervision of the late E. R. Ward.[360,361] This early work also sparked an interest in substituent effects, which was to develop later into Wells' work on linear free-energy relationships.[362–365] He then spent 1958/1959 at Iowa State doing postdoctoral work with C. H. de Puy. Wells arrived at the University of Queensland to take up a Lectureship just in time for the 1959 Christmas party. He intended to study aromatic brominations and, in a search for other electrophilic substitutions, decided to examine mercuration reactions. **Bill Kitching** (see below) was Wells's first Ph.D. student, and commenced work on the mercuration of aromatics. The nature of the interaction of mercury salts with acetic acid was at that time unclear. Wells and Kitching demonstrated by synthetic, ^{1}H NMR and $J_{^{199}\mathrm{Hg}-\mathrm{H}}$ means that a mercurated acetic acid polymer with Hg–C bonds is produced.[366–369]

V. G. Kumar Das (now Professor of Inorganic Chemistry at the University of Kuala Lumpur) commenced work with Wells at this time, and began by examining long-range coupling in organolead compounds on the University's newly acquired A60 NMR machine.[370] Hexamethyl- and hexaphenyl-lead were then commercially available, and Wells commenced a general programme of investigation of the relative reactivities of M–M and M–C bonds in Group 14 organometalloids. These studies encompassed organolead[371–378] and organotin compounds (particularly the reactions of $[\mathrm{Me_6Sn_2}]$, with $[\mathrm{Me_2SnCl_2}]$ or [MeHgX] or $\mathrm{HgCl_2}$ in methanol),[379–384] as well as mixed Sn–M (M = C, Si, Ge) derivatives[385–388] and have involved kinetic and mechanistic studies, product analysis, multinuclear and INDOR NMR. Wells also collaborated with Don McWilliam (now at the Tasmanian State Institute of Technology, Launceston), Dennis Arnold (now at the Queensland University of Technology) and Matthew Cuthbertson (now with Sola Optical).

Wells received his D.Sc. from the University of London in 1976. Since the mid-1980s his research has been dominated by his interest in aromatic organic chemistry.

Bill Kitching was introduced to organometallic chemistry in 1960 as part of his Ph.D. studies under the supervision of Dr Peter Wells at the University of Queensland. This work consisted of physical organic and ^{1}H NMR studies of aliphatic organomercurials,[389–391] which were of increasing importance in the general field of electrophilic aliphatic substitution (S_E reactions). On receipt of a Fulbright Fellowship, Kitching spent an initial period with Professor Ray Dessy at Cincinnati. Dessy had a developing interest in the electrochemistry of organometallic compounds and 'subvalent' species. They examined a range of organomercury, -tin, and -lead derivatives and generated solutions of anionic species which were examined spectroscopically and by derivatization.[392–395] Kitchings interest in reaction mechanisms of Main Group organometallics developed further, and he and Dessy produced a chapter on 'Organometallic reaction mechanisms' for *Advances in Organometallic Chemistry*.[396]

Kitching then secured a postdoctoral position with the late Professor S. Winstein at UCLA, and worked on the palladium(II) oxidation of olefins.[397] This stimulated his interest in the general area of oxymetallation of alkenes, and the interesting behaviour of σ- and π-allyl derivatives of metals, and led to the proposal that allylic oxidation of olefins in acetic acid by $[Pd(OAc)_2]$ proceed by reversible oxy-palladation and elimination of $[HPd(OAc)]$.[398]

On his return to the University of Queensland, Kitching decided that mechanistic studies of the formation and cleavage of carbon–metal bonds was a promising field, as such steps were thought at the time to be implicated in many metal-catalysed reactions. This also led to an interest in the coordination chemistry of organometallic cations, particularly of alkyltin systems such as $[(CH_3)_3Sn]^+$ and $[(CH_3)_2Sn]^{2+}$, etc.[399–401] and also of Pd(II).[402] To explore the chemistry of allylic derivatives more carefully, Kitching's group have concentrated particularly on the σ-allyl derivatives of tin and mercury and π-allyl palladium compounds.[403,404] Insertions of SO_2 into C–Sn bonds were examined in collaboration with Dr Clifford Fong, and shown to proceed with allylic rearrangement, and also allenic–propargylic rearrangement in appropriate systems.[405] Electrophilic cleavage by the simplest electrophile, H^+, of carbon–metal bonds has been of continuing interest,[406,407] and the regio- as well as stereo-chemistry have been determined in suitable cases. For example, in suitable 5-alkylcyclohex-2-enyl derivatives of tin, acid cleavage proceeds highly preferentially by *anti* approach of the electrophile to the γ-carbon of the allylic triad and there is a stereochemical rationale for these S_E2' reactions.[408,409] Studies of the formation of carbon–metal bonds, e.g. by reactions of stannyl- and germyl-anionoids, have also been conducted in this area, and the involvement of single electron transfer shown in some cases, particularly of alkyl bromides and iodides.[410,411]

With the availability of multinuclear NMR facilities, structural studies of organometallics rapidly developed. When Dr Bill Adcock took up a post at the Flinders University of South Australia, he and Kitching undertook a collaborative study on the substituent effects of metal and —CH_2–metal groups attached to various aromatics. This was based largely on ^{19}F and ^{13}C NMR spectroscopy. Some remarkable effects were identified, particularly the very strong σ–π donor effects of CH_2M even in the ground state.[412–416] This work led indirectly to studies of the conformational preferences of metalcontaining groups attached to cyclohexanes. Detailed studies of mercury-containing groups (some in conjunction with Professor F. A. L. Anet at UCLA, and Professor D. Doddrell, now at the University of Queensland) established a slight, but definite, preference for the axial orientation, the only known group with such a preference.[417,418] The conformational preferences of various Group-14-based moieties have also been determined.[419–421] An earlier collaboration with David Doddrell (then at the University of New England, Armidale, New South Wales) of various organometallics led eventually to the finding of *vic*-coupling (^3J) between ^{119}Sn and ^{13}C. This was independently recognized by Henry Kuivila at Albany, New York, and led to a joint publication with him on the angular dependence of $^3J_{^{119}Sn\text{–}C}$.[422] This dependence has been of major importance in structural and conformational studies of organostannanes.[423–425] Subsequently, a similar dependence was established for ^{119}Hg–^{13}C coupling[426] and this has also been widely used in organomercury chemistry.

In conjunction with other interests, the use of organomercurials in synthesis, particularly of spiroacetal systems, has been developed,[427,428] and the very interesting organometallic chemistry of medium and larger cycloalkanes and cycloalkenes are being examined. The use of oxidation of Main Group carbon–metal bonds, e.g. of tin and mercury, is increasing, and a chapter for *Comprehensive Organic Synthesis* in this area has been completed.[429]

Another of Wells's early students, **Bill Adcock** [B.Sc. (Hons.) 1961, Ph.D. 1965], began his Ph.D. by examining substituent effects in substituted naphthalenes.[430–432] Adcock obtained postdoctoral appointments at the University of Texas (1965–1966) and CSIRO, Melbourne (1966–1967) before joining the Flinders University of South Australia. He, Bill Kitching and Dave Doddrell established an extensive collaborative programme examining the substituent effects of organometalloid moieties such as MMe_3, HgAr, $Tl(O_2CCF_3)_2$, CH_2Si, $RMMe_3$, Me_3Sn, Ph_3MCH_2, etc. (M = Group 14 atom; R = alkyl, aryl, furyl, thienyl) by ^{13}C and ^{19}F NMR.[412–416,433–437] The chemical shifts and coupling constants were shown to be useful in making structural and stereochemical assignments. Adcock is now a Reader in Chemistry and Dean of the School of Physical Sciences at the Flinders University of South Australia.

Leon Kane-Maguire completed a B.Sc. (Hons.) degree at the University of Queensland in 1964, investigating geometric and optical isomerism in octahedral cobalt(III) complexes under the supervision of Dr Tom McDermott. His Ph.D. thesis (University of Queensland, 1967), under the supervision of Dr John Broomhead, involved the synthesis of halo–amine ruthenium(III) complexes, and kinetic and spectroscopic studies of their substitution reactions.

Two years' postdoctoral research with Professors Ralph Pearson and Fred Basolo at Northwestern University, Illinois, was also in the area of coordination chemistry, involving synthetic and mechanistic studies of molecular nitrogen and nitrene complexes. However, a subsequent 15-month postdoctoral period with Professor Jack (now Lord) Lewis first at University College London and later at Cambridge caused him to change his major research interest to organometallic chemistry.

In 1971, Kane-Maguire joined the faculty at University College Cardiff in Wales, where his research largely concerned synthetic and mechanistic studies of the reactions of coordinated hydrocarbon ligands. A long-standing collaboration in this area with Dr Dwight Sweigart of Brown University began following a visit to Cardiff by Dr Sweigart in 1976.

A growing interest in asymetric synthesis and chiral discrimination in organometallic systems was further catalysed by a sabbatical leave in 1983 at the Australian National University working with Martin Bennett. This visit also led to continuing collaboration in this area with Bruce Wild of the Australian National University.

Following his appointment as Professor of Chemistry at the University of Wollongong in late 1983, Leon Kane-Maguire has developed a strong collaboration with Dr Stephen Pyne into asymmetric synthesis with π-hydrocarbon complexes. More recently, a sabbatical leave with Professor Lewis at Cambridge has led to a growing involvement in mechanistic studies of metal clusters.

THE AUSTRALIAN NATIONAL UNIVERSITY

In 1960, **Martin Bennett** obtained his Ph.D. at Imperial College, London under the supervision of Professor Geoffrey (later Sir Geoffrey) Wilkinson and Dr (now Professor) E. W. Abel. His thesis was entitled 'Olefin and carbonyl complexes of the transition metals'. There followed a postdoctoral appointment at the University of Southern California from 1960 to 1961 working with Professor Arthur Adamson on the photochemistry of transition metal complexes. Bennett was appointed Turner and Newall Fellow at University College, London from 1961 to 1963. While there, he worked with Professors Nyholm and Lewis on metal complexes of chelating olefinic tertiary phosphines and arsines. Bennett also collaborated with Glen Robertson and Richard Bramley who were at University College at this time. Bennett, Bramley and Robinson were eventually all to join the Research School of Chemistry, Australian National University. In 1963, Martin Bennett was appointed a Lecturer in Chemistry at University College, London. On 2 and 15 March 1965, respectively, Wilkinson *et al.*, and Bennett and Longstaff submitted notes describing the synthesis of $[Rh(PPh_3)_3Cl]$, its reactions with hydrogen and alkenes, and its conversions to $[Rh(PPh_3)_2(CO)Cl]$ (by reaction with CO, OAc^- or allyl alcohol) and $[Rh(PPh_3)(diene)Cl]$(diene = norbornadiene, cycloocta-1,5-diene).[438] Exactly a year later, Wilkinson's group submitted their seminal paper on the catalytic reactions of Wilkinson's catalyst, $[Rh(PPh_3)_3Cl]$.[439] Martin Bennett moved to the Research School of Chemistry, Australian National University as a Fellow in 1967, becoming a Senior Fellow in 1970, and a Professorial Fellow in 1979.

Martin Bennett's research interests have centred on transition metal complexes containing carbon, and Group V donor ligands. A substantial portion of this work has been concerned with the formation of cyclometallated complexes.[440] The most outstanding example is the iridium(I) complex $[IrCl(PPh_3)_3]$, which spontaneously transfers a hydrogen atom from the *ortho* position of one of its triphenylphosphine ligands to the metal.[441,442] Bennett's group has also developed methods for the generation of σ-alkyl complexes of the transition metals by novel oxidative addition reactions. Key elements in this endeavour have been the discovery of stable platinum complexes of a highly unstable, short-lived acetylene, cyclohexyne,[443,444] which oxidatively add water under mild conditions, and stable nickel complexes of the short-lived molecule benzyne, which undergo a range of insertion reactions.[445,446] Bennett's research has also been concerned with the rearrangements which occur in σ-alkyls of the transition metals, both in monodentate and chelate systems.[447] An extensive chemistry of aromatic complexes of ruthenium has been developed.[448–450] These complexes are useful precursors to a variety of hydrocarbon complexes of zerovalent and divalent ruthenium, some of which are catalytically active. Bennett's more recent work involves the chemistry of dinuclear metal complexes, some of which contain a bridging cyclometallated ligand,[451] the preparation of platinum(II) hydroxycarbonyls,[452] and investigations into the activation of the C–H bond.

Martin Bennett was awarded a D.Sc. by the University of London in 1974, the Royal Australian Chemical Institute's H. G. Smith medal in 1977, and the Royal Society of Chemistry's Award for the Chemistry and Electrochemistry of Transition Metals in 1981. He was elected a Fellow of the Australian Academy of Science in 1980, and delivered the G. J. Burrows Lecture of the Inorganic Chemistry Division of the Royal Australian Chemical Institute in 1987.

It is fitting that this section on Australian organometallic chemistry should conclude with the work of **S. Bruce Wild**. Turner introduced organoarsenic chemistry to Australia in 1919 and Wild can be considered to be the person who has developed the earlier work of Turner to its extreme in a stereochemical sense, often with the use of the basic coordination chemistry of tertiary arsines elucidated by Nyholm and his co-workers. Wild's group in the Australian National University has developed highly stereoselective syntheses of optically active and diastereomerically homogeneous tertiary arsines and tertiary phosphines.[453,454] Sophisticated ligands based on these elements have been prepared for use in asymmetric synthesis. This work has included the stereoselective synthesis of macrocyclic bis(tertiary arsines), and the synthesis of poly(tertiary phosphine) macrocycles and cages, as well as the production of optically active tertiary arsines by biological methods.

In 1964 Wild completed a B.Sc. (Hons.) degree at the University of New South Wales. His honours project involved syntheses of tertiary arsine derivatives of titanium(IV) and zirconium(IV) halides under the supervision of Gordon Barclay and Ian Gregor. This work included the study of $[Ti(triars)X_4]$ compounds.[455] Barclay and Nyholm had earlier prepared $[NiBr_2(triars)]$—the first five-coordinate nickel compound[456,457]—the structure of which was determined by Powell and co-workers.[458] Wild was another young Australian chemistry graduate of the 1960s to travel overseas to obtain a higher degree. He joined Professor (later Lord) Lewis's group in the University of Manchester, and worked on metal–metal bonded organometallics for his Ph.D. (1967).[459] While in Manchester, Wild and Lewis collaborated with Arthur Birch on the chemistry of cyclohexadiene iron tricarbonyls.[34] Birch (1967) and Wild (1980) eventually joined the Research School of Chemistry of the Australian National University, and Wild returned briefly to the study of diene iron tricarbonyls in collaboration with Leon Kane-Maguire in 1982, while the latter was at University College Cardiff. In 1968, Wild spent a postdoctoral year as an Alexander von Humbolt Fellow with E. O. Fischer in Munich, and then returned to England to University College London, where he again worked as a postdoctoral fellow, this time with another expatriate Australian, Brice Bosnich, on the resolution of chiral tertiary arsines by metal complexation.[460,461] He went with Bosnich to the Lash Miller Chemical Laboratories of the University of Toronto for one more year before taking up a Lectureship in the University of Western Australia in 1970. Since 1980, he has been on the staff of the Research School of Chemistry of the Australian National University, where he is currently a Senior Fellow. Inorganic stereochemistry and asymmetric syntheses continue to dominate Wild's research interests; a recent development has been the asymmetric synthesis of chiral glycerol derivatives with the use of an optically active bis(tertiaryphosphine)-

platinum(II) auxiliary, and the isolation of platinum(II) complexes of simple alcohols, including sugars.

THE NEW ZEALAND SCENE

In the meantime, the development of organometallic chemistry in New Zealand was no less vigorous. New Zealand's proud tradition in inorganic chemistry was carried overseas by the likes of Barrer, Clark, Reed and Reid. One of the central figures in organometallic chemistry in New Zealand was Cuth Wilkins of the University of Canterbury. His students and colleagues include Andrew Brodie, Brian Robinson and Warren Roper. Robinson, Roper, Simpson, Nicholson and Duffy are all represented in the present collection.

Eric Ainscough completed his B.Sc. (Hons.) and Ph.D. degrees under the supervision of Professor R. Plowman of the University of Queensland. Ainscough's Ph.D. work was on the coordination chemistry of bulky phenanthrolines, and this was completed in 1968. He then went to Simon Fraser University, British Columbia, to work with L. K. Petersen on the synthesis and coordination chemistry of systems containing P–N bonds. Then he moved to King's College, London, to work with S. D. Robinson on intramolecular metallation reactions of a series of triphenylphosphites. In 1971 he was appointed as a Lecturer in Inorganic Chemistry at Massey University in New Zealand, where he has collaborated with Andrew Brodie on various research projects, including some that were organometallic-oriented. This partnership is still in existence and their research interests are quite varied.

Andrew Brodie is a graduate of the University of Canterbury, New Zealand. He obtained his B.Sc. (Hons.) degree in 1965 and his Ph.D. in 1968. He worked under the supervision of Profesor C. J. Wilkins and Dr G. A. Rodley using far-infrared spectroscopy to probe the coordination chemistry of ligands containing arsenic, antimony and bismuth with the first-row transition elements. He was then awarded an SRC Fellowship to work with Professor Jack (now Lord) Lewis and Dr B. F. G. Johnson at University College London. It was here that he was introduced to rhenium and iron carbonyl chemistry. In 1970 he was appointed to a Lectureship in the Department of Chemistry and Biochemistry at Massey University where is now an Associate Professor. He was soon joined by Dr Eric Ainscough, and together they have established an active and fruitful collaboration. Much of their work has been concerned with the interaction of sulphur ligands with transition elements, and has included research into organometallic and coordination compounds as well as the blue copper protein, azurin. More recently, they have been concerned with copper-promoted reactions of sulphur-containing molecules. Collaboration with Professor Ted Baker's protein crystallography group has led them to study the spectroscopic properties of the iron-binding protein, lactoferrin, from human milk. This work was described by Brodie in the 1987 Liversidge Lecture presented to the ANZAAS Congress in Palmerston North. In 1976, Brodie spent ten months in Japan on a Japanese Ministry of Education Fellowship working with Professor Sei Otsuka on copper chemistry. The award of a Nuffield Fellowship in 1982 allowed him to renew his contact with the Lewis–Johnson group at the University of Cambridge where he worked on osmium carbonyl cluster chemistry. He returned to Cambridge in 1989 for another 12 months working in the same area.

Ken Mackay completed his B.Sc. (Hons.) degree at the University of Aberdeen in 1957 and went on to work with Professor Harry J. Emelèus at the University of Cambridge for a Ph.D. In 1960, he went to the University of Nottingham, first as an Assistant Lecturer, and then as a Lecturer in the Inorganic Chemistry Department under the leadership of Professor C. C. Addison. In 1970, he was appointed as Reader in the newly founded School of Science at the University of Waikato, Hamilton, New Zealand, and was appointed Professor in 1978, following the resignation of the foundation Professor, Alec Wilson. He has spent six years of the following period as Head of Department.

At Cambridge, Ken Mackay's Ph.D. study was concerned with the reactions of covalent hydrides with sodium in liquid ammonia. This led to an interest in the properies of germanium hydrides, particularly in materials which contained the germanium–germanium bond. At that time, element–element bonds for the metallic and semimetallic elements were thought to be unusual and unstable. Work at Nottingham developed a chemistry of substituted digermanes, and of related species containing Ge–Ge and Ge–Si bonds, and led eventually to the synthesis of other germanium–metal-bonded species containing a number of metal atoms and of Group 14 atoms. In recent years at Waikato, this work has developed substantially involving spectroscopic and crystallographic characterizastion and the evolution of a number of synthetic approaches, many involving the hydride. Work has also continued on germanium compounds, especially in the exploration of ^{77}Ge NMR.

After graduating M.Sc. (Hons.) in chemistry in 1962, **Brian Robinson** carried out Ph.D. research with Jack Fergusson and Cuth Wilkins at the University of Canterbury. This was his first encounter with metal clusters—in this case halo clusters of molydenum and rhenium. Upon graduation in 1965, he went to Newcastle upon Tyne, working with Norman Greenwood on borane chemistry and then, in 1966, to Manchester with Jack Lewis. Here, an accidental discovery of some manganese and ruthenium clusters, during his work on the kinetics of carbonyl substitution, switched his interests back to cluster chemistry, which he continued when appointed to the University of Otago in 1967. Work on the capped clusters $[YCCo_3(CO)_9]$, showed that these molecules had a rich chemistry which formed the basis of his research for a number of years.

Jim Simpson graduated B.Sc. (Hons.) in chemistry at the University of Southampton in 1964. He continued at Southampton, working with John Drake on the chemistry of Group 15 derivatives of silicon and germanium hydrides and their reactions with borane Lewis acids, completing a Ph.D. in 1967. He was awarded an SRC postdoctoral fellowship at the University of Sussex to work with Mike Lappert, using mass-spectroscopic measurements to obtain thermodynamic data on compounds containing metal–metal bonds.

In 1969, he took up a Lectureship at the University of Otago in Dunedin, New Zealand, and continued his interest in organo–transition metal chemistry with work on polysilyl derivatives of the transition metals and the coordination chemistry of Group 7 carbonyl halides. Shortly after his arrival at Otago, Simpson undertook to learn the art of X-ray crystallography under the expert guidance of Ward Robinson of the University of Canterbury. Structural determinations, using data obtained from the Christchurch difractometer, have remained a major interest, and have contributed significantly to the development of his work in organometallic chemistry.

A confluence of interests in metal carbonyl chemistry saw the beginning, in 1971, of a long-term collaboration with Brian Robinson in the field of organometallic cluster chemistry. In particular, the redox chemistry of cobalt clusters proved particularly fruitful with the discovery that clusters of the type $[YCCo_3(CO)_9]$ (and subsequently a variety of their isolobal analogues) formed unusually stable and strikingly reactive radical anions. These novel radicals were found to initiate facile substitution, isomerization and metal transfer reactions. Their collaborative work in this field was enhanced by a number of visitors to Otago, of whom Phil Rieger, Ron Dickson, Alan Bond and Heinrich Vahrenkamp made particular contributions to developments in this area. Work on the electrochemistry of cluster compounds took a new turn with the discovery that cations derived from ferrocene-capped tricobaltcarbon and tricobalt bis-carbyne clusters undergo intervalence transfer processes. The potential of such systems in the field of unidimensinal semiconductors has led to a continuation of work on a variety of potential mixed-valence systems containing metal clusters linked by ferrocenyl groups, alkyne chains, or a combination of the two.

In 1987, interest in the use of ferrocenyl ligands sparked a new, joint research initiative in the field of cytostatic metal complex chemistry. The preparation of ferrocenylamine and phosphine derivatives of platinum(II) has revealed a wealth of intriguing chemistry and produced a number of compounds showing promising activity against specific murine tumours.

Warren R. Roper completed his B.Sc. (1960), M.Sc. (1961) and Ph.D. (1963) degrees at the University of Canterbury under the direction of C. J. Wilkins. He worked on an electron diffraction study of an organosilicon compound, rhenium chemistry, and Main Group organometallic chemistry. A period of postdoctoral research with Professor J. P. Collman at the University of North Carolina, Chapel Hill, NC, USA, confirmed him as a transition-metal organometallic chemist. He returned to New Zealand to a Lectureship at the University of Auckland in 1966, where he developed oxidative addition reactions, particularly of nitrosyl compounds. In 1972, Roper spent a sabbatical leave in Professor F. G. A. Stone's laboratory in Bristol where he further developed an interest in metal–carbon bonds. This interest later grew to include metal–

carbon triple bonds, reduced carbon monoxide fragments as ligands, and the stabilization of reactive molecules through coordination to Platinum Group metals. He was appointed Professor of Chemistry at Auckland in 1984. Warren Roper was the Pacific West Coast Lecturer in 1982, and has held visiting Professorships at Leeds, Rennes, and Stanford Universities. In 1984, the Royal Society of Chemistry recognized his work by the Organometallic Chemistry Award, and in 1989 he was the RSC Centenary Lecturer. He was elected to the Royal Society of New Zealand in 1984, and to Fellowship of the Royal Society (London) in 1989.

Joyce Waters completed her M.Sc. (Hons. 1) degree in chemistry in 1955 under the supervision of F. J. (later Sir John) Llewellyn at Auckland University College (now University of Auckland). A Ph.D. in inorganic crystallography followed, initially under the direction of F. J. Llewellyn and later with D. Hall. In 1958, Joyce spent a year in the crystallographic group of J. Chatt at the ICI Akers Research Laboratories in Hertfordshire, England, where she undertook the X-ray structural analysis of the hydrido complex, [Pt(PEt$_3$)$_2$HBr], that had been prepared by Chatt and B. L. Shaw. A move to the Atomic Energy Research Establishment at Harwell followed in 1959. In 1961, she retuned to the newly created University of Auckland as a Lecturer in Chemistry. Her interests were mainly in structural inorganic chemistry and in the 1970s and early 1980s she collaborated with Warren Roper and his group in the same Department on structural aspects of organometallic complexes, particularly those of carbenes and carbynes. A move to Massey University, Palmerston North, was made during 1983, where she became interested first in structural aspects of cluster chemistry and more recently in metalloboranes containing π-bound aromatic rings. Joyce has also spent periods of study leave in Dorothy Hodgkin's laboratory at Oxford investigating the structure of vitamin B$_{12}$ derivatives (the coenzyme vitamin B$_{12}$ was one of the early organometallic complexes characterized by the X-ray method) and in Jim Iber's laboratory at Northwestern University, Evanston, Illinois, USA.

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