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Alan Cowley was one of the most creative main group chemists of his generation, and
had a central role in what was often described as the renaissance of main group chemistry.
Throughout his career Alan always had an eye for what was new. In his early years as
an independent researcher, Alan made many fundamental contributions to the chemistry of
phosphorus, not only in terms of the synthesis of new compounds but also in their study
by employing novel analytical and computational methods. Starting in the 1980s he was
at the forefront of emerging research into low-coordinate phosphorus chemistry and made
seminal contributions in the areas of multiply bonded species, such as phosphonium ions and
diposphenes, as well as in the transition metal coordination chemistry of phosphinidenes.
In the second half of his career, Alan also turned his attention to the study of single source
precursors for important solid-state electronic materials, many of which were far superior to

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known examples. In all of the many areas in which Alan worked, he was a great collaborator with colleagues and researchers across the world, both in chemistry and in other disciplines. This was made all the easier by Alan’s charm and easy-going nature, which was also manifest in the interactions he had with his many group members over a period of almost half a century. Alan was a gentleman in every sense and is much missed by friends, colleagues, collaborators and family.

**EARLY LIFE, EDUCATION, INDUSTRY, TRAVEL AND FAMILY**

Alan Cowley was born in 1934 in Manchester, England, to Herbert and Dora (née Smalley) Cowley. Alan’s father had been an ambulance driver and stretcher-bearer for the Red Cross during World War I, but after the war he became a travelling salesman, measuring for and selling men’s suits, and so was part of the drapery trade. Alan’s mother worked as a bookkeeper, but also at one time found employment in the soap-making industry with Unilever at Port Sunlight.

At the start of World War II Alan was five years old. His sister, Stella, was born in 1941 and, at times when German bombing raids made living in the central Manchester area unsafe, they were evacuated to live with families in the Yorkshire countryside. Alan’s father remained in Manchester during these episodes, saying that ‘if Jerry didn’t get him in World War I they wouldn’t get him now’.

Alan’s early school life was therefore fragmented by wartime disruptions and his education no doubt suffered as a result, causing him to fail the 11+ exam twice (this was the UK’s exam that would determine whether a pupil aged 11 years would attend a secondary modern school or a more selective grammar school). After the first failure, his mother petitioned his school for him to retake the exam since she believed there had been a mistake in the grading (‘He’s a bright lad’). Alan promptly failed it a second time, which meant that he did not qualify to attend any of the local Manchester area grammar schools. Despite this setback, however, Alan’s mother was determined that he should receive a good education and managed to obtain a non-academic scholarship for him to attend Russell School (now Royal Russell School) in Croydon near London. At that time the school operated with generous donations from members of the drapery trade, and, since Alan was the son of a draper, he was duly admitted.

Alan did not squander his second chance and excelled in many subjects, including languages, winning the French prize one year. The headmaster at Russell School at that time was F. A. V. Madden (MA/Oxon), a graduate of the University of Oxford, and Alan’s outstanding oral and writing skills in the English language were no doubt due to the teaching and influence of Mr Madden. When it came time for him to choose a subject to study at university, Alan’s best subjects were the Classics (Latin and Greek) and chemistry. His first choice was to study Latin and Greek, but his mother explained to him that he would not be able to make a living with a degree in Classics. Her chemistry background at the soap factory was enough to convince Alan that that was the subject he should study, and he was subsequently accepted to read chemistry as an undergraduate at the University of Manchester; he graduated with a BSc in 1955, followed by an MSc in 1956 and a PhD in 1958. His doctoral thesis, under the direction of Professor F. Fairbrother, was focused on the halides of the Group 5 (then Group VA) elements Nb and Ta (1)*.

* Numbers in this form refer to the bibliograpy at the end of the text.
After completing his PhD, Alan decided that a sunnier climate was called for and he accepted a postdoctoral position (1958–1960) at the University of Florida under the mentorship of Professor Harry Sisler where he studied derivatives of borazine six-membered rings containing B–Si bonds. In those days international travel was not for the common man and Alan’s first journey to the United States was by sea aboard an industrial freighter carrying approximately 20 fare-paying passengers to Jacksonville, Florida, the journey being made possible by a generous gift from his uncle, Thomas Smalley, inventor of the TS electrical switch. Despite the less-than-ideal travel arrangements for this first trip to the New World, Alan developed a love for travel and during the course of his career visited many countries to give lectures and/or to participate in meetings or workshops. His preferred mode of transport was soon to become a first-class seat with American Airlines, but Alan’s love of travel would not be confined to the airline industry. He also had an enduring interest in cars, and over the years owned a number of classic British and German sports cars, several of which were given names as a sign of affection. The first of many was a three-litre Austin Healy, which he bought from his University of Texas (UT) at Austin colleague William (Bill) Wade, followed by an MG, a vintage Chevrolet (The Blue Goose) and a Volkswagen (Klaus). In his later years he owned two very fine Porsches (a 944 and a 911) and several Mercedes Benz. Despite having been keen on motorcycles during his Manchester years, once at UT, Alan, perhaps wisely, decided against any further involvement with two wheels, at least as far as ownership was concerned, although he would occasionally ask for (and usually be granted) ‘a go’ on a motorcycle owned by one or other of his group. A picture of Alan that brings together both cars and American Airlines is shown in figure 1.

During his time carrying out postdoctoral research, Alan met Maria Elena Sancho Castro, from Costa Rica, and his flair for language enabled him to rapidly learn conversational Spanish. After the completion of his postdoctoral work, the couple returned to the UK and were married in 1960, their first child, Peter, being born in 1961. It was here that Alan began a career as an industrial chemist with ICI (1960–1962), and during this time his progress in the company was described as ‘good enough for middle management’. The idea of middle management did not sound attractive, however, and Alan again decided to seek opportunities in the US by sending a handwritten application for an assistant professorship position to Dr Norman Hackerman, who was at that time the chairman of the Chemistry Department at UT Austin. Not long after, Alan received a telephone call from Hackerman, who simply asked: ‘Well, are you coming?’ He accepted immediately. Unlike today, there was no formal interview, no departmental seminar, no faculty discussion and no democratic vote involved in Alan’s hiring. Hackerman had simply trusted his instincts and took a chance on hiring a junior colleague. In order to fulfil certain visa requirements Alan returned to the US via a short stay in Costa Rica, this time travelling by air. His academic career at UT Austin thus began in 1962.

At that time there was no air conditioning in UT’s chemistry building and the brutally hot Texas summers meant that experiments had to be carefully planned, although hot summer afternoons were often spent cooling off at Barton Springs, a local spring-fed swimming pool. The family grew with the births of David (1962) and Alison (1967); however, there were strains in the marriage and Alan and Maria Elena separated and later divorced, in 1972. It was a very difficult and sad time for both of them, but after a five-year period of bachelorhood, Alan met Deborah Cole and they were married in 1977. Deborah became a very successful businesswoman who founded, and ran for many years, Greater Texas Landscapes, a landscape
The University of Texas at Austin and professional activities

Alan’s academic career at UT Austin would span some five decades from 1962 until his formal retirement in 2015. It was briefly interrupted in 1988 when he accepted the prestigious Sir Edward Frankland Chair of Chemistry at Imperial College London. This chair had become vacant owing to the retirement of Sir Geoffrey Wilkinson FRS (Nobel Prize 1973), but Alan and Deborah did not settle in London, and he was lured back to UT Austin a year later after being offered the Welch Chair of Chemistry, a position previously held by Michael J. S. Dewar FRS.

Alan’s kind and generous personality enabled him to develop a great rapport with the members of his research group. Weekly group meetings were lively affairs, when the latest results would be discussed and recent literature analysed. These would often be followed by a trip to a local bar (often paid for by the students and postdocs!) so that the discussions could be continued in a more relaxed setting. Alan was also highly regarded by UT undergraduate
students for the enthusiasm he displayed during his lectures, and he continued to teach classes throughout his career. For relaxation, Alan enjoyed squash and, during his time at UT, became a very fine squash player, playing well into his seventies. Regular partners included many of the chemistry faculty, as well as Norman Hackerman, who by then had become president of the university.

In addition to his research and professional activities associated with UT, Alan became heavily involved with the Gordon Research Conferences (GRC) in the 1980s. He was originally introduced to the unique format of the conferences when he attended an inorganic chemistry GRC in the mid 1960s. He described this experience as (21):

> a career-influencing event in every respect. I had never attended a meeting with such lively, abundant discussion. Moreover, the informal ambience encouraged both new friendships and meaningful interactions with several distinguished inorganic chemists whose work I had read and admired. I became an aficionado of GRC, and with Alex Cruickshank’s encouragement, I got involved with the organization’s management.

He served as an elected member of the GRC council from 1984 to 1987 and was a member of the Selection and Scheduling Committee from 1988 to 1989. He then served on the GRC board of trustees from 1989 until 1998. During this period the organization underwent significant change, which included consideration of the question of internationalization. The implementation of this change involved Alan and Carl Storm, the GRC director, visiting many prospective overseas conference sites and dealing with the inevitable diplomatic issues that
arose. The travel was greatly enjoyed. In addition, Neil Gordon, founder of the GRC, had
made many contributions to science education and was founding editor of the American
Chemical Society’s *Journal of Chemical Education*. The board of the GRC was therefore
naturally concerned with science education and, during his first term on the board, along with
Paul Saltman, Alan helped to organize the first Science Education Gordon Conference.

Alan’s many interests also encompassed the commercial applications of chemistry and
material science. Besides his adventures in Chile (see below), he consulted occasionally for
PPG Industries Chemicals Division, which reminded him of his early days at ICI. He was
also an investor and/or scientific advisor to several development-stage companies, including:
Systine, a semiconductor etching tool company in Pasadena; Materia, a company co-founded
by Bob Grubbs (ForMemRS 2017) around his Nobel prize-winning ruthenium catalyst; and
Convergent Ventures, a seed-stage life sciences fund in which Alan was an investor as well
as acting as an advisor to two of its companies, Neurion Pharmaceuticals, an ion channel
technology spun out of Caltech, and ORFID, a printable semiconductor company spun out
of UCLA. Alan was always a lively contributor to these nascent businesses, enjoying the
interactions with scientists, business advisors and company staff, and always generous in
providing good ideas and helping to find solutions to their problems.

The following sections outline some of Alan’s most important contributions to chemistry
and materials science throughout his career as well as giving a flavour of his approach to
undertaking research.

**EARLY PHOSPHORUS AND RELATED MAIN GROUP CHEMISTRY**

Alan’s PhD work on the chemistry of the Group 5 metals Nb and Ta (Group VA as they were
then known), coupled with the interest he had developed in main group elements such as B,
S and Si while carrying out postdoctoral work with Harry Sisler, led Alan to focus much
of his early research at UT on the related Group 15 (then called Group VB) elements N, P
and their heavier congeners. At the time this was a daring move since main group chemistry
was not particularly fashionable in the US, transition metal chemistry research being much
more dominant. While there certainly were US-based research groups working in non-metal
chemistry, notably the groups of Earl Muetterties, Bob West, Bob Parry, Bob Holmes, Anton
Burg and Fred Hawthorne, it is fair to say that research groups in Europe were much more
prominent in the field, in particular the UK—for example, Mike Lappert (FRS 1979), Evelyn
Ebsworth, Norman Greenwood (FRS 1987), Ken Wade (FRS 1989), Colin Eaborn (FRS 1970)
and Gordon Stone (FRS 1976)—and Germany—including Didier Astruc, Herbert Roesky,
Rolf Appel, Edgar Niecke, Reinhold Schmutzler, Alfred Schmedipeter, Hubert Schmidbaur,
Egon Wiberg, Wolfgang Malisch and Peter Jutzi. For this reason, all of the early graduate
students and postdoctoral fellows in Alan’s group were required to have at least a rudimentary
understanding of scientific German!

Another consequence of main group chemistry being in its early stages in the US required
that Alan search far and wide for potential collaborators and, in looking back over his long
career, it is obvious that one of Alan’s main strengths as a researcher was his ability to
collaborate with his UT colleagues. It is unlikely that anyone published with more colleagues
than did Alan, particularly important collaborations being with Michael Dewar, Allen Bard,
Dick Lagow, Ray Davis and (most notably) Richard Jones. Important collaborations would
also be developed with other US-based researchers such as Al Cotton (ForMemRS 1994), Malcolm Chisholm (FRS 1990), Kurt Mislow, John Verkade and Jerry Atwood, as well as with esteemed international scientists such as Didier Astruc, Herbert Roesky, David Rankin, Evelyn Ebsworth and Peter Jutzi. Alan’s students would greatly benefit from interacting with such a diverse cadre of eminent scientists.

The majority of the research carried out in Alan’s group for the first 15 or so years of his career centred on phosphorus chemistry and ranged from structural studies of P(V) compounds to the isolation and characterization of novel low oxidation state and low-coordinate species. One particular topic investigated during the early years was the nature of P–P and P–N bonding. Alan’s innate curiosity led him to examine these problems in what would now be called a holistic fashion in order to understand everything he could experimentally, using a wide range of analytical techniques in combination with computational studies. Although it may be difficult to imagine in today’s world, it should be remembered that the mid to late 1960s was a period when basic multinuclear nuclear magnetic resonance (NMR) studies, for example, and computational chemistry, were very much in their infancy. A perusal of Alan’s publications in these early years reveals a large number that dealt with the NMR spectra of main group compounds and an important subset of these papers were quite fundamental in nature, dealing both theoretically and experimentally with the signs of $^1J$ coupling constants, among them $^{31}$P–$^1$H, $^{31}$P–$^{31}$P, $^{31}$P–$^{15}$N, $^{31}$P–$^{19}$F, $^{31}$P–$^{29}$Si and $^{29}$Si–$^{19}$F couplings. From these studies, much could be and was learned about the nature of these particular bonding interactions.

While Alan’s early work on the structures of cyclopolyphosphines ([RP]$_x$) and cyclopolyarsines ([RAs]$_x$) using NMR spectroscopy made a noteworthy contribution, perhaps his years-long and wide-ranging investigations into understanding the fundamental nature of P–N bonding, and then using these aminophosphines in more complex synthetic chemistry, is the most complete illustration of his efforts in the early years. For example, several of Alan’s papers in this area were directed at understanding the interactions between the two lone pairs of electrons associated with the P–N bond (one on each atom) and the resulting restricted rotational barriers as measured by dynamic NMR studies. One classic contribution with Michael Dewar corrected two erroneous literature studies and proposed that the low-temperature limiting structures of aminophosphines (Me$_2$N)PR$_2$ contained a nearly planar N atom (1 and 2) in a gauche conformation compared with a pyramidal N atom (3) in a more symmetrical anti conformation, as had been previously postulated (figure 3) (2). This initial report led to many more publications dealing with P–N bonding and provided important background knowledge concerning N-containing substituents in P, Si and S compounds, especially in cationic species—which would later evolve into a study of two-coordinate phosphorus cation chemistry, which itself would subsequently establish a gateway into the even more novel low-coordinate Group 15 chemistry featuring element–element double bonding.

Thus, while numerous projects involving P(V) chemistry continued, the chemistry of low-coordinate main group compounds would come to dominate Alan’s research during the mid 1970s and well into the double bond era in the 1980s (see below). Some of the early synthetic and characterization work on N-silyl substituted aminophosphines, later to become important as polyphosphazene polymer precursors, was begun at this time, and during these investigations it was recognized that the lone pair on the N atom substituent might stabilize a P(III) cation (a so-called phosphenium ion isoelectronic with both a neutral carbene and
Figure 3. Newman projections of selected P–N compounds, 1–3, referred to in the text. In each case the P atom is not shown and lies behind the N atom. In 1 and 2, the N lone pair effectively resides in an unhybridized p orbital (not shown) orthogonal to the N trigonal plane.

Figure 4. The relationship between carbene, silylene and phosphonium species, showing the lone pair in an sp² hybrid orbital and a vacant p orbital orthogonal to the R₂E plane (E = C, Si, P).

a neutral silylene) as a result of π-donation to the vacant orbital on P (figure 4). This was demonstrated in 1978 when X-ray quality crystals of the compound [(Pr²N)₂P][AlCl₄] (4), containing the phosphonium ion [(Pr²N)₂P]⁺, were prepared by simple halide abstraction from the starting chlorophosphine using AlCl₃ (10). An X-ray crystallographic study not only confirmed the structure but showed a shortening of the P–N bonds consistent with substantial π-donation from N to P as well as revealing a nearly planar C₂N–P–NC₂ framework. While initially it was believed that two amino substituents were required to stabilize a phosphonium ion, later work showed that one of these could be replaced with a sterically demanding Bu group affording a phosphonium ion with a ³¹P NMR chemical shift of 513 ppm, which at the time was the most deshielded ³¹P chemical shift ever measured, demonstrating the inability of the Bu group to donate electron density to the P centre. Later, other electron-donating groups, including ferrocenyl (Fc) and cyclopentadienyl, were used as substituents to prepare stable phosphonium ions, a selection of which are shown in the legend of figure 5. The same synthetic strategy of halide abstraction was also employed to successfully prepare the related S(IV)-based dications. However, despite significant efforts, attempts to prepare a stable silicenium ion, [SiR₃]⁺, analogous to carbenium ions (carbocations) were not successful and instead resulted in N–Si donor–acceptor complexes with the Lewis acidic AlCl₃ rather than halide abstraction.

Interestingly, since phosphonium ions possess both a lone pair and an empty p orbital on the P centre, it was expected that they should be able to function chemically as both a Lewis acid and a Lewis base. Work carried out by various members of Alan’s group did indeed show that these phosphonium ions could function as specialized two-electron donors towards other Lewis-acidic phosphines or to transition metal complexes. In a useful synthetic strategy, these cations were also shown to react readily at low temperatures with 1,3-dienes to form
Figure 5. The reaction between chlorophosphines \( \text{PClR}_1\text{R}_2 \) and \( \text{AlCl}_3 \) to afford phosphonium ions: 
\( \text{R}_1 = \text{R}_2 = (\text{Me}_3\text{Si})_2\text{N} \) or \( \text{Me}_2\text{N} \); 
\( \text{R}_1 = \text{Me}_2\text{N}, \text{R}_2 = X \) (where \( X = \text{Cl}, \text{Bu}^t, \text{C}_5\text{Me}_5, \text{Fc} \); 
\( \text{R}_1 = \text{R}_2 = \text{Fc} \); 
\( \text{R}_1 = \text{R}_2 = \text{Pr}^t\text{N} \).

Figure 6. The reaction between the phosphonium ion \([\text{P(NMe}_2\text{)}_2]^+\) and 2,3-dimethylbuta-1,3-diene affording a cationic phosphorus heterocycle, 5. The anion, not shown, is \([\text{AlCl}_4]^–\).

Five-membered phosphorus heterocycles that were difficult to prepare by other methods; an example is shown for the heterocycle 5 in figure 6 (12). Lastly, these P(III) phosphonium ions were later shown to mimic carbenes by undergoing oxidative additive reactions with the \( \text{C}–\text{H} \) bonds of bis(cyclopentadienyl)metal complexes to form, among other compounds, P(V) metallocene-substituted phosphonium ions.

**Multiple Bonding and the Heavier Main Group Elements**

In W. E. Dasent’s monograph *Nonexistent compounds* (Dasent 1965), molecules of the heavier p-block elements featuring \( \pi \text{–}\pi \) multiple bonding merited a chapter to themselves. Ongoing efforts to prepare such species continued without success, which led, perhaps not surprisingly, to what became known as the ‘double bond rule’, which stated that such compounds were too unstable to be isolated. An early glimpse that matters might be about to change came in 1976 with the isolation of the first stable, non-conjugated phospha-alkene compound featuring a phosphorus–carbon double bond (\( \text{RP=CR}_2 \)), but this was to be just a prelude to the early 1980s, after which the ‘double bond rule’ was comprehensively refuted and consigned to history. Thus, 1981 saw the isolation of the first stable phospha-alkyne (\( \text{RC≡P} \)) and the first disilene (\( \text{R}_2\text{Si=SiR}_2 \)) containing a phosphorus–carbon triple bond and a silicon–silicon double bond respectively, and the following year brought reports of a stable sila-alkene (\( \text{R}_2\text{Si=CR}_2 \)) and a stable diphosphene (\( \text{RP=PR} \)), the former containing a silicon–carbon double bond and the latter a phosphorus–phosphorus double bond. It would be to the chemistry of the last of these examples, the diphosphenes and their heavier Group 15 congeners, that Alan would make a very significant contribution. As Alan and others would go on to demonstrate in a
series of seminal papers, in all of these examples, the key to their isolation was to make the organyl R group sufficiently sterically demanding that formation of cyclo-oligomeric compounds containing the thermodynamically more stable element–element single bonds was prevented; as noted earlier, Alan had previously studied cyclopolyphosphines, [RP]x, which were examples of these more stable species.

The diphosphene 6, the first of its class, had been reported in 1981 by Yoshifuji’s group in Japan (Yoshifuji et al. 1981), but the following year Alan published a paper that corrected an erroneous 31P NMR chemical shift in the original report (the correct value was 494 ppm) together with the synthesis of a second example of a diphosphene, 7 (5). Both compounds had been prepared by the reductive coupling of precursor dichlorides, RPCl₂, but in 1983 Alan would demonstrate (6) that a synthetic method that involved the coupling of the species RPH₂ and R’PCl₂ enabled the first unsymmetrical diphosphene, 8, to be prepared, thereby allowing a direct measurement of the 1J₃₁P–3₁P NMR coupling constant (577.5 Hz; ¹J values for RP values for RP=PR are typically around 5–600 Hz). Perhaps more importantly, however, Alan would show in two further papers that by using the arsenic analogues RAsH₂ and R’AsCl₂, a stable diarsene 9 could be synthesized (7) and, moreover, that by reacting a dihydrido phosphine species RPH₂ with an arsenic or antimony dichloride R’ECl₂ (E = As, Sb), stable examples of a phospha-arsene, 10, and a phosphastibene, 11, could be prepared (8), as shown in figure 7.

In the space of just a few years, several papers followed on the properties and reactivity of diphosphenes in particular (14). Many X-ray structures were reported (including a detailed electron density study), along with NMR spectroscopic studies, both in solution and in the solid state, as well as electrochemical data on oxidation and reduction. Investigations into the reactivity of diphosphenes, and also of diarsenes, with numerous electrophiles and nucleophiles were described, but one particular class of reaction studied was an examination of diphosphenes and diarsenes as ligands in transition metal complexes. It was already known, for example, that transition metal complexes of diphosphenes could be isolated, even in situations where the R groups were too small to allow the isolation of the uncoordinated diphosphene itself. Several examples had been characterized in which the phosphorus lone
pairs and the \( \text{P=P} \) π bond were shown to coordinate to a metal centre either individually or in combination, as shown in 12 in figure 8. In a series of studies, Alan demonstrated that isolable diphosphenes and diarsenes would coordinate to metal centres, but usually with just one metal fragment coordinated owing to the steric bulk of the \( \text{R} \) groups (14). Two examples, 13 and 14, are shown in figure 8.

**TRANSITION METAL ‘INIDENE’ COMPLEXES**

The reason for highlighting the coordination chemistry of diphosphenes and diarsenes is that this chemistry would be the start in Alan’s group of a more general exploration of the chemistry of transition metal complexes of low-coordinate main group species. Specifically, complexes containing an \( \text{RE} \) fragment, where \( \text{E} = \text{P, As, Sb} \) and \( \text{R} \) is an organyl group, are generally referred to as ‘inidenes’, \( \text{RP} \) being a phosphinidene, for example. Several examples of phosphinidenes, and their heavier congeners, coordinated to two or more metal centres were already known, but there were no examples of so-called terminal inidene complexes in which the \( \text{RE} \) fragment was coordinated to a single metal centre. Alan would write about the search for a terminal phosphinidene as a ‘quest’ (15) and it is interesting to briefly recount the journey that would ultimately lead to a successful outcome.

In a 1985 paper (11), Alan described the reaction between the iron carbonylate anion \([\text{Fe}_2(\text{CO})_8]^{2-}\) and the antimony dichloro species \(\text{SbCl}_2[\text{CH(SiMe}_3)]_2\) that afforded compounds 15 and 16, the former being an \(\text{Fe(CO)}_4\) complex of a distibene and the latter a di-iron compound with a bridging stibinidene. A paper a year later (13), which explored the analogous tungsten chemistry, described another example of a stibinidene complex, 17, and it is clear from the diagrams of 16 and 17 that two possible structural forms are possible for a bridging stibinidene, the so-called ‘closed’, 16, and ‘open’, 17, forms (figure 9), in which the \(\text{Sb} \) centre is trigonal pyramidal and trigonal planar, respectively.

A series of papers from 1985 to 1988 explored the related chemistry of ‘closed’ and ‘open’ bridging phosphinidene complexes, the general distinction between which is shown graphically in 18 and 19 in figure 10, and the reasons why one or other structure might be adopted, but, despite many attempts, an isolable terminal phosphinidene complex remained elusive.

There was, however, a compound that Alan had reported in 1984 (9), namely the phosphavinylidene complex, 20, which, although not a phosphinidene complex, was tantalizingly close to the target of the quest. As it would turn out, the first stable terminal phosphinidene complexes, 21, would be reported by Mike Lappert in 1987 (Hitchcock et al.
Figure 9. Distibene, 15, and stibinidene, 16 and 17, complexes.

Figure 10. Representations of ‘closed’, 18, and ‘open’, 19, phosphinidene complexes. The phosphorus centre in 18 is trigonal pyramidal with a localized lone pair on the phosphorus whereas in 19 the phosphorus is trigonal planar and the lone pair is de-localized across the metal–phosphorus–metal (MPM) unit.

Figure 11. Phosphavinylidene, 20, and terminal phosphinidene, 21 and 22, complexes.

1987), but three years later, in 1990, Alan would describe (17) the second example, 22, and the first to exhibit a linear geometry at phosphorus as opposed to the bent geometry seen in Lappert’s compounds (figure 11). A number of examples from other groups would follow in the next few years, allowing Alan to write about the ‘quest’ being over in 1997 (19).

As a footnote to the story of terminal phosphinidenes, in 1998 Alan would turn his attention from phosphorus to boron and published a report (20) of the first terminal borylene complex, 23 (figure 12), which, along with the isolation of a number of metal–boryl species, LnMBR2, at around this time would usher in a renaissance in the chemistry of low-coordinate boron fragments coordinated to transition metal centres.
In 1986, Alan began a very productive collaboration with his colleague, Richard Jones, on the synthesis and analysis of III–V (13–15) compound semiconductors. Richard had been working on bulky phosphido complexes of the d-block metals and became aware of a funding opportunity provided by the State of Texas: the Texas Advanced Technology Research Program. Although sources within the chairman’s office at that time advised them not to bother as ‘there was very little chance of success’, with a very short deadline for submission, Alan and Richard put together a remarkably concise proposal of three to four pages, including references. It was fully funded to the tune of US$650,000, and this funding enabled basic research to advance rapidly such that by 1990 there were enough preliminary data to justify the establishment of one of the National Science Foundation’s first science and technology centres. The multidisciplinary collaborative research programme, entitled Synthesis, Growth and Analysis of Electronic Materials, involved up to 14 UT scientists in chemistry, physics, and chemical and electrical engineering, and received continuous funding for over 12 years. The work was founded on a simple concept. A volatile compound, which involved a direct covalent bond between the Group 13 and 15 elements, might serve as a useful precursor to thin films of solid-state materials such as gallium arsenide (GaAs) or indium phosphide (InP), which were of key importance to the microelectronics industry. The two examples, 24 and 25, shown in figure 13 were among the very best precursors to GaAs and InP respectively (16, 18).

**Photoelectron spectroscopy**

Reference has already been made to Alan’s extensive collaborations and to his use of a broad range of experimental and analytical techniques alongside computational studies. One technique in particular in which Alan was an early pioneer was gas-phase ultraviolet (UV) photoelectron spectroscopy (PES), which warrants its own highlight since Alan’s contributions were so influential. Alan’s opinion regarding this technique is best summarized with a quote from the abstract of an early review article that he published concerning PES in relation to bonding in phosphorus chemistry (3):
Figure 13. Precursor compounds for GaAs, 24, and InP, 25.

No attempt will be made to infer that pes [PES] is a deus ex machina capable of functioning as the final arbiter on all controversial bonding problems; rather the general tenor will be one of unbiased examination of a selection of currently unresolved questions with a recently developed tool.

The technique of PES was pioneered initially by Vilesov in (then) Leningrad, but most of the early work that led to the wide acceptance of this method was developed by David Turner (FRS 1973) in the 1960s, first at Imperial College London and later at the University of Oxford (Turner 1970). In a gas-phase UV photoelectron spectrometer, molecules are ionized with monoenergetic UV photons, most commonly from the He 584 Å (21.22 eV) emission line. The spectrum is obtained by measuring the kinetic energies (KE) of ejected electrons and plotting intensity versus energy (usually in eV). From the conservation of energy relationship, \( KE = h\nu - I_n \) (where \( I_n \) is the ionization or binding energy), a series of so-called ‘bands’ are obtained which correspond (ideally) to the energies of the occupied valence molecular orbitals.

Around 1970, Perkin Elmer began producing the PS-18 instrument, the first commercial gas-phase UV photoelectron spectrometer, and researchers around the world now had access to this powerful technique. As has been noted earlier, Alan had a strong interest in phosphorus compounds, many of which were volatile (important for a gas-phase technique) and featured lone pairs on phosphorus which are easily identified in a photoelectron spectrum.

Alan’s PS-18 would arrive in early 1977, but he had no intention of waiting that long to explore the potential of the technique. Working with Michael Dewar, one of whose PhD students, D. Wayne Goodman, had built a PES spectrometer, a series of six PES papers were published in the early 1970s, all centred around bonding in phosphorus compounds. The first concerned the geometry around the nitrogen atom in P–N bonds (see section ‘Early phosphorus and related main group chemistry’), with the last sentence of the paper suggesting that the structure of tris(dimethylamino)phosphine should be reinvestigated, since their PES results suggested a symmetry lower than three-fold. This was followed by a detailed study of the bonding in phosphorus pentafluoride, determination of gas-phase trans/gauche isomers in diphosphines and diarsines, \( \pi-\sigma \)-bonding (or, rather, the lack of it) in polyphosphines, torsional barriers in aminophosphines and, finally, the effects of trifluoromethyl substituents in phosphines and chlorophosphines. These early studies were a clear demonstration of Alan’s skill at utilizing this new technique to gain further insights into the many topics of his research at that time.
Shortly after these initial reports, the PS-18 instrument arrived, and Mike Lattman, who had studied PES in his PhD research, joined Alan’s group. Collaboration with Dewar nevertheless continued and new collaborations with John Verkade, Al Cotton and Malcolm Chisholm were begun. The association with Verkade was particularly fruitful, leading to five papers describing conformation and basicity of acyclic, cyclic and caged phosphites, thiophosphites and aminophosphines. With Cotton, PES studies probed the bonding of complexes containing metal–metal quadruple and triple bonds, while bonding in dialkylamino metal complexes was examined with Chisholm. Alan extended his PES studies to include cyclopolyphosphines, conjugation effects in phosphorus chemistry, phosphine basicity and bonding in sulfur tetrafluoride and its derivatives, as well as π-complexes of transition metals and main group elements.

Perhaps the most unexpected publication to appear during this time was Alan’s comprehensive review article on PES in transition metal chemistry in 1979 (4). This was the most complete review of the topic at that time, although no one would classify Alan as a transition metal chemist—but this again demonstrates his ability to quickly learn a new field, most likely inspired from his collaborations with Cotton and Chisholm.

Many of the papers that focused on experimental PES data were combined with molecular orbital calculations, primarily MNDO (modified neglect of diatomic overlap) for main group elements and Xα-scattered wave for the transition metals, the synergy between molecular orbital calculations and experimental PES data being crucial to the interpretation of the spectra. Indeed, from the earliest stages of his career, Alan was a strong proponent of combining experimental and analytical work with the most up-to-date calculational methods in order to gain the maximum insight into new molecules to better understand their structures and reactivity. Often this would be in collaboration with expert groups such as that of Michael Dewar, but Alan frequently employed computational chemists in his group and made full use of UT's computing facilities.

**Later work**

Alan continued his prolific scientific publishing record until well into his eighties, and this account of his research has focused on only a few of his primary research areas. However, always interested in new ideas and new chemistry, over the years Alan published papers in a variety of different areas, which included studies on boron arsenide, stable N-heterocyclic carbenes, metal complexes of bis(imino)acenaphthene (BIAN) and luminescent electropolymerizable metal complexes and corresponding conducting metallopolymers.

Besides all the new chemistry, another important feature of Alan’s career was the ‘human product’, which resulted from the number of chemists who trained and learned directly under him. The vast majority of these chemists, his graduate students and postdoctoral fellows, have themselves gone on to distinguished careers in industry, national laboratories and the academic world. To a person, all would greatly credit their overall success to their time spent in the Cowley laboratory being mentored by a world-class researcher who was never short of ideas, interest or enthusiasm. Indeed, the research efforts of all of those who were at one time members of Alan’s group are a lasting legacy to his contributions in chemistry and materials
science. A picture taken at his formal retirement event in Austin in 2015 with some former group members is shown in figure 14.

**CHILE**

Alan’s love of travel has already been noted, but he especially enjoyed travel to South American countries, where his Spanish speaking ability was put to good use. He was particularly fond of Chile, not least because a former PhD student, Miguel Mardones, had founded a small business in Santiago (Pacific Chemical Ltda) which employed Alan as a scientific and technical advisor. The company designed, fabricated and installed industrial gas washing systems for the elimination of toxic and objectionable odours that are produced by industrial processes, one of the most important applications of the technology being in the mining industry. Chile is one of the major producers of copper, and processing the ores produces significant quantities of sulfur-containing gases that have to be removed from waste gas streams before they can be vented to the atmosphere. Mining operations take place in the north of the country in the high elevations of the Andes mountains, and Alan relished site visits to these remote and spectacular locations. A photograph taken during one such visit is shown in figure 15.
Throughout his career, Alan played a pivotal leadership role in inorganic chemistry not only at UT but also, as mentioned earlier, through his involvement with the Gordon Research Conferences. During this time, he established himself as one of the leading figures in the renaissance of main group chemistry and authored over 500 peer-reviewed publications in the chemical literature. Alan's specialty, as will be clear from the outlines above, was the
chemistry of the Group 15 elements phosphorus, arsenic and antimony, and his pioneering work in the field was recognized by his receipt of numerous awards, including a Guggenheim Fellowship (1976), the Royal Society of Chemistry Award for Main Group Chemistry (1980) and the American Chemical Society Award for Distinguished Service in the Advancement of Inorganic Chemistry (2009). Alan received the order of Chevalier dans l’Ordre des Palmes Academiques from the French government in 1977 and was elected a Fellow of the Royal Society in 1988.

We end this memoir with a quotation from the author James A. Michener, which featured in the programme for Alan’s retirement colloquium in 2015 and which we all believe captures Alan’s essence particularly well; he always referred to chemistry as his hobby as well as his profession. To quote Michener is all the more apt since he lived his final years in Austin and, as one of us (RAJ) recalls, he and Alan would occasionally meet in the UT Austin Faculty Club.

The master in the art of living makes little distinction between his work and his play, his labor and his leisure, his mind and his body, his information and his recreation, his love and his religion. He hardly knows which is which. He simply pursues his vision of excellence at whatever he does, leaving others to decide whether he is working or playing. To him he’s always doing both.

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The portrait photograph is used with kind permission from The University of Texas at Austin. We also thank Miguel Mardones for the information about Alan’s endeavours in Chile.

AUTHOR PROFILES

Richard A. Jones
Professor Richard Jones is an emeritus professor at The University of Texas at Austin, USA. He recently retired from the university, where he was a professor of chemistry. He received a BSc in chemistry in 1976 and a PhD in 1978, both from Imperial College London. His PhD mentor was Sir Geoffrey Wilkinson. After two years as a postdoctoral research fellow with Sir Geoffrey, he joined The University of Texas at Austin as an assistant professor in 1980. He was promoted to associate professor in 1986 and to full professor in 1988. During his time at Austin, he established a very productive collaborative research programme with Alan Cowley.

Richard A. Kemp
Professor Rick Kemp is an emeritus professor at the University of New Mexico (UNM), USA. He recently retired from dual half-time positions at UNM and Sandia National Laboratories, where he was a principal member of the technical staff. He received his BS degree in chemistry at Texas Tech University in 1978, working under the direction of Professor Jerry Mills, one of Alan Cowley’s first PhD graduate students. Rick was so enamoured of main group chemistry research that he chose to attend graduate school at The University of Texas at Austin for his PhD under the mentorship of Cowley, receiving his degree in 1982. After spending ca. 20 years working in industrial oil and chemical catalysis, where he commercialized various heterogeneous catalyst systems, he returned to more fundamental studies in synthetic inorganic/organometallic chemistry and homogeneous catalysis while at UNM/Sandia.

Jonathan G. Lasch
Jonathan G. Lasch is the executive director for the Alfred E. Mann Institute for Biomedical Engineering at the University of Southern California, USA. Additionally, he serves as senior faculty advisor for the Fully Employed
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Michael Lattman
Professor Michael Lattman is professor of chemistry at Southern Methodist University, Dallas, USA. His formal education was obtained at The City College of New York, where he received a Bachelor of Science degree (chemistry) in 1972, and at The City University of New York, where he received a Doctor of Philosophy degree (inorganic chemistry) in 1977 under the direction of Professor Michael A. Weiner. From November 1976 until August 1979 he was a postdoctoral research fellow at The University of Texas at Austin carrying out research with Professor Alan H. Cowley. In September 1979 he joined the faculty of the Chemistry Department at Southern Methodist University, where he currently holds the tenured position of professor of chemistry.

Nicholas C. Norman
Professor Nick Norman CChem FRSC is professor of inorganic chemistry in the School of Chemistry at the University of Bristol, UK. He obtained a BSc in chemistry in 1979 and a PhD in chemistry in 1982, both from the University of Bristol. He was a postdoctoral research associate at The University of Texas at Austin from 1982 until 1984, where he worked with Alan Cowley, and returned to the UK to become temporary lecturer in inorganic chemistry at the University of Manchester (1984–1985). He was lecturer then reader at the University of Newcastle upon Tyne from 1985 to 1995 and since 1995 has been at the University of Bristol, being promoted to professor of inorganic chemistry in 2006. His interests are in synthetic inorganic chemistry, particularly in the chemistries of boron and bismuth, and in chemical education.

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