## Professor Malcolm Green FRS (1936–2020)

### Septcentenary Fellow and Tutor in Inorganic Chemistry 1963–1989 and Emeritus Fellow from 1991

Professor Geoff Cloke (1971 and Junior Research Fellow 1979)
Andrea Sella (1986)

Malcolm Green was a larger-than-life chemist who burst on to the Balliol scene in 1963, having been elected as Septecentenary Fellow and Tutor in Inorganic Chemistry at the comparatively young age of 27. He graduated from Acton Technical College (where, he used to proudly say, he hadn't graduated with a First) but Malcolm's love of organometallic chemistry began when he joined the research group of Geoffrey Wilkinson at Imperial College as a PhD student. Wilkinson had recently returned from Harvard, where, in parallel with R.B. Woodward, he established the 'sandwich' structure of ferrocene, two parallel 'slices' of cyclopentadiene (a five-membered organic ring) held together by an atom of iron. Malcolm prepared molybdenum, tungsten, and rhenium analogues before setting out on his own at Cambridge as a Research Fellow at Corpus Christi College, where the brilliant polymath Christopher Longuet-Higgins (1941) was a Fellow. Malcolm's three years in Cambridge were extraordinarily productive and he established his reputation for creativity, churning out molecules with unusual structures. He also developed a reputation as something of a wild man. Hugely extrovert, with an unfiltered passion for his subject, he would bring samples to his lectures to show to his students

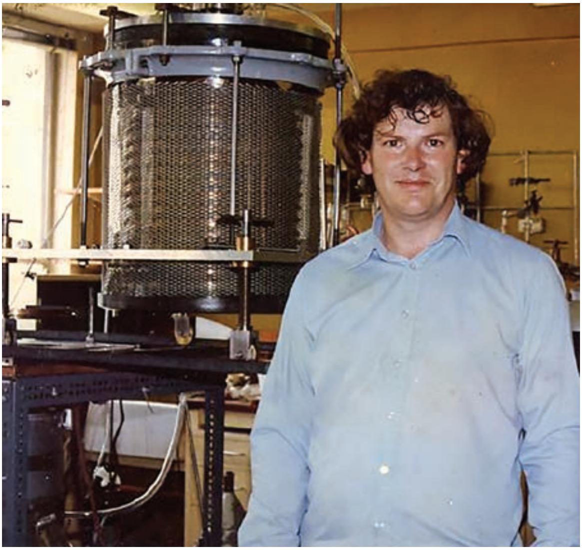
When Malcom started at Balliol, he lived in College and had a set at the top of Staircase XXI. His rooms were dominated by a large obviously homemade model of ferrocene, and were somewhat chaotic – a feature he put to good use when explaining the concept of entropy to first-year students. As a tutor, Malcom was unconventional, but inspirational. He would usually arrive late for tutorials, having rushed to College straight from the lab, and immediately tell us about his latest discovery before moving slightly reluctantly on to drier subjects such as the radius ratio rules or the Kapustinskii equation. Our weekly essays were returned eventually, occasionally bath-damaged and always covered in Malcolm's mostly illegible scrawl, with a rather impenetrable grading based on the Greek alphabet. This was of course before the days of written student 'feedback', but it didn't matter to us. What did matter was Malcolm's obvious passion and enthusiasm for the subject. It would be fair to

Modelling the characteristically baggy jumpers he favoured, at the farm in the mid-1970s.

say that Malcolm didn't really play an active role in College admin, although he was (and he would say this with a glint in his eye) 'Tutor for Married Graduates' and, significantly, an enthusiastic and proactive member of the small committee that led to Holywell Manor becoming Balliol's hub and community for postgraduates.

Malcolm's lectures to undergraduates, given in often dishevelled but wildly enthusiastic fashion without notes, and his conference contributions, both intellectual and social, would become the stuff of legend. Malcolm was the epitome of the 'work hard, play hard' mentality. The sense of his mastery of his subject was enhanced by the fact that he peppered his lectures with molecules whose properties came to life so vividly as to almost have personalities.

This extraordinary familiarity with the organometallic world came from a set of mental pictures that helped him to 'see' what was normal and humdrum as opposed to where the real action was. He would often joke that 'to a first approximation all transition metals are the same' while at the same time having



In the lab with his giant MVS machine in 1980.

an instinctive and nuanced sense of the differences between them. In the late 1970s, working with his wife Jenny, who provided the theoretical rigour, Malcolm developed these mental pictures into a formal scheme that came to be known as MLX or CBC (Covalent Bond Classification). By classifying the groups of atoms (ligands) attached to a metal and considering how many electrons were associated with it, the MLX scheme generated a map that summarised the behaviour of each metal. Suddenly one had a visual representation of what chemistry was common and what was unusual, rather than a dry list; Malcolm's heuristics were now available to all. The scheme was first presented in a series of lectures while he was on sabbatical in Paris in 1972 and subsequently at Harvard in 1973. Further refinements benefited from collaboration with Ged Parkin, a former student and now a Professor at Columbia. The method has been adopted in undergraduate teaching because of its simplicity and internal consistency, as well as its ability to make sense of some very varied chemical terrain.

With Steve Davies and Mike Mingos, Malcolm also developed a set of, today eponymous, rules that help chemists predict the position at which certain chemical reagents will attack rings or chains of carbon bound to a transition metal. These foundational ideas are today in every textbook and lie at the heart of the use of transition metals in organic synthesis, with huge implications for pharmaceuticals and drug synthesis.

Malcolm's early fascination with organometallic sandwich compounds increased apace when he moved to Oxford, where he made molecules with a variety of ring sizes and developed their reactivity. Chemical synthesis of this kind is typically conducted in a series of steps where the groups of atoms surrounding a metal atom (the ligands) are added, replaced, or modified sequentially to arrive at the desired final product. In 1970, Peter Timms from Bristol gave a lecture in Oxford where he described a new way of making organometallics. Timms' idea was to vaporise metals into highly reactive individual atoms and then to let these strike the walls of a flask cooled to the temperature of liquid nitrogen (approx. –200 ˚C) together with another substance. Thus, the synthesis of a sandwich compound of chromium and benzene would simply involve firing atoms of chromium into an 'ice' made of frozen benzene. It was like having delicate tweezers that allowed you to pick up an atom and slip it between rings of carbon.

Malcolm immediately saw this as a way of making hitherto inaccessible sandwich complexes of highly refractory metals like tungsten and tantalum. This was not going to be easy, since vaporising those metals (once used for the filaments of incandescent light bulbs) requires temperatures in excess of 3000 ˚C. He sought the advice of his physical chemistry colleague at Balliol, David Turner (Emeritus Fellow), who pointed him in the direction of a company called G.V. Planar, who provided him with an electron beam furnace. This marked the beginning of a long and succesful collaboration; the company funded several DPhil students in Malcolm's group (including one of the authors) to develop and scale up the technique, and subsequently sold several metal vapour synthesis (MVS) machines worldwide based on Oxford designs.

The experiments were spectacular to watch. A huge bell-jar almost 2 feet across was surrounded by a cylindrical tank filled with liquid nitrogen and then evacuated to ultra-low vacuum. Once the walls were sufficiently cold the molecular 'bread' was sprayed on to the walls and the power was turned up on the furnace. A blinding white glow from the incandescent metal bead was projected on to the ceiling of the lab through a frothing lake of liquid nitrogen. The light would slowly change to yellow, orange and red, like a sunset, as the frozen chemical matrix built up. This was often the moment for Malcolm to appear with a visitor to show off his pride and joy. No visitor left disappointed.

For all its macho extremism, MVS would prove an unusually delicate synthetic technique that uncovered a vast menagerie of new molecules, each of which could then be reacted in myriad ways. The vast majority of these molecules were extremely ‘electron rich’, molecules likely to lose electrons so easily that some were even capable of attacking the normally inert dinitrogen, N2. This work took Malcolm in a very different direction from that of ‘rival’ research groups in Britain (vide infra). Many of the DPhil. theses from Malcolm’s group can be summarised with schemes looking like a hub with spokes: at the centre, a single highly unusual MVS product, and radiating arrows pointing to the myriad products obtained with anything and everything that could be found in the group’s chemical store room. With exploratory work like this, surprises were never far away.

Inevitably, Malcolm’s research touched on one of the great chemical challenges of the 1980s, the breaking of C–H bonds, known in the field as C–H activation. Until then, the alkanes, the saturated hydrocarbons that make up the bulk of crude petroleum, were an unloved backwater of organic chemistry. Their high symmetry and uniform charge distribution gave the arsenal of the organic chemist little purchase on these molecules. Selective transformative chemistry was rare outside the industrial cracking processes that underpin the petrochemicals industry. Seen as rather dull, these alkanes could either be used as solvents, or they could be burned destructively as fuel. It was a challenge hiding in plain sight.

In the 1960s, there had begun to be hints that C–H bonds could be attacked selectively using transition metal compounds, especially when these were ‘electron rich’. Thus, Malcolm’s avoidance of the classical carbon monoxide ligand, favoured by research groups in Bristol and Cambridge, opened new opportunities; Malcolm and his students pushed the limits of electron richness as far as they could. In doing so, numerous surprises came to light. Handling such species was not for the faint-hearted, and required exceptional technical skills along with a robust attitude to risk. After one fire in the lab, one of the firemen leaving the site was overheard to mutter ‘Malcolm Green. Explosion machine.’

The group not only uncovered many examples of this C–H activation, but they also isolated examples of a class of molecules in which a C–H bond seemed to sit in a kind of suspended animation, close to the metal but without actually being split. With academic visitor Maurice Brookhart, Malcolm identified the molecules as key evidence to account for how C–H bonds were broken by metal centres. His Balliol colleague Jasper Griffin (1956, Dyson Junior Research Fellow 1961–1963, Tutorial Fellow in Classics 1963–2004) (who, echoing Flanders and Swann, immediately christened Malcolm the ‘the Gas Fellow’ when he was awarded a prestigious Royal Society British Gas Fellowship in 1979) suggested the Homeric word ‘agostic’ to describe

Lecturing in Venezuela.

these interactions. The term stuck, much to the disgust of Malcolm's highly competitive American contemporary F. Albert Cotton (ironically Geoffrey Wilkinson's first American PhD student), who believed that he, and he alone, should be credited with the discovery. Malcolm just ignored Cotton. Despite continuing rear-guard action by autocorrect software, the word 'agostic' is now in the Oxford English dictionary. Malcolm and Brookhart proposed that agostics might play a key role in catalysis, especially the mechanism of the spectacularly efficient Ziegler-Natta catalysts that assemble the plastics polythene and polypropylene that we take for granted in our lives; in their view delicate agostic interactions might help control the orientation of incoming substrate/monomer molecules and control the growing chain of polymer. The proposal would inspire a number of exquisitely elegant experiments conducted by several of Malcolm's old friends and collaborators that gave the ideas ample support.

Malcolm ran a large research group, which at its height, in the 1980s, comprised around 30 students, typically three or four undergraduate 'Part IIs', 15–20 postgrads, three or four postdocs and a handful of academic visitors. The topics explored were often very varied, with students having considerable freedom to explore their own ideas. Students were assigned a bench in the labs on the north side of fourth floor of the Inorganic Chemistry Lab (ICL), each equipped with a standardised vacuum line and a set of drawers in which the day-to-day equipment such as clips, clamps, valves, stopcocks, stoppers, rubber bands and the like was organised using the remains of plastic chemicals jars, rinsed out and cut in half. There were few fume hoods, so students worked on the open bench except for unusually large-scale or exceptionally smelly reactions.

At the start of the academic year there would be a general clean-up and tidying of the lab, a useful exercise to orient new arrivals who might find themselves helping to catalogue the group's chemical store (a dark and horribly smelly Aladdin's cave of more and less useful chemicals). They would them be asked to conduct large-scale 'preps' of key starting materials, an unforgettable, multi-day baptism of fire overseen by more experienced students (the 'old lags'). For example, the preparation of the diphosphine 'dmpe-tetrachloride' took place in an ancient, Baskerville autoclave starting with tens of grams of white phosphorus, several hundred mls of the highly corrosive $PCl_3$ and 'a handful of iron nails', the brew pressurised with ethylene and heated to 150 °C. The fire when the reaction vessel was rinsed out usually attracted a small but excitable crowd of voyeurs. The preparation of Malcolm's favourite compound from his PhD, $Cp_2WH_2$ started with a pair of 3-litre flasks sitting side-by-side in a baby bath filled with crushed ice, stirred energetically with a pair of mechanical stirrers. The student added finely ground starting materials from two other flasks through wide-bore plastic hoses while Malcolm stood not far away poking steel needles through the hoses to keep the powder from clogging.

Malcolm was a hands-on kind of supervisor who would typically emerge from his small and cluttered office at the far end of the hallway; reading glasses perched on top of his head and his pipe clamped between his teeth, he would come through the labs in the late afternoon each day cheerily asking 'What's new?' For students, these visitations could be moments of amusement or dread, as Malcolm might well take over whatever they were doing – part of a synthesis or a solvent evaporation – sometimes using his cigarette lighter to assist things. The results could be mixed. On his retirement in 2003, former students assembled 'Chairman Malcolm's Little Green Book', a collection of hilarious (and sometimes terrifying) reminiscences of some of the highlights of their time in the lab.

Thursday evenings were reserved for the group meeting in the Abbot's Kitchen, where a couple of students would report on their latest results or on an interesting recent paper they had found in the literature. For some this was terrifying, as they might not have much to report (synthetic chemistry can be brutally frustrating). And also because there might be questions, both from

Malcolm and Jenny and from other members of the group who might chip in with ideas. These meetings would then transfer seamlessly to the King's Arms, where ideas would continue to be sketched out on beermats; Malcolm was never short of an idea or three. While some ideas did not survive scrutiny in the cold light of the morning, others would be filed away for a Friday afternoon experiment. Eventually, and somewhat reluctantly, Malcolm would have to leave the KA to return home (which was a College house just round the corner in St Cross Road, next door to John Jones (1961 and Emeritus Fellow) and Maurice Keen (1954 and Fellow and Tutor in Modern History 1961–2000, Emeritus Fellow 2000–2012) and their families), but not before he had left a generous wad of cash on the table to encourage the festivities to continue. Friday mornings were typically rather subdued.

In 1985 Malcolm was elected Fellow of the Royal Society. Asked by a student whether he would therefore be joining the Athenaeum Club next door, he replied, 'Don't be silly. I'm buggered if I'm going to pay £1,500 a year for the privilege of drinking at £4 a pint with some old bishops.' It was pure Malcolm. In 1989 he succeeded the solid-state chemist (and later Nobel Prize winner) John Goodenough as head of the Inorganic Chemistry Lab (ICL). The position being linked to St Catherine's College, he had to resign from his Tutorial Fellowship at Balliol and therefore move out of St Cross Road to a new house in North Oxford, which two of his students helped to refurbish in exchange for free lodgings for a couple of years. For Malcolm it was something of a wrench, because of his deep affection for Balliol, where most of his students continued to be based; he was delighted to be elected an Emeritus Fellow in 1991 and regularly took his lunch in the SCR, so in a sense he never really left.

His tenure as head was not always easy given the very high profile and strong personalities of some of his colleagues. A key challenge was to ensure that the ICL maintained a broad portfolio of scientific interests and remained well funded. He also had to contend with the heads of the other chemistry labs, including Jack Baldwin (whom Malcolm nicknamed 'the suburban barracuda' on account of his unfortunate lack of hair and his approach to both science and University politics) of the Dyson Perrins Lab with whom he had cordial, but testy, relations. Malcolm's students were largely oblivious to this, apart from a reduction in the frequency of his visits to the lab now that his office was two floors below. But in spite of his administrative duties, constant proposal-writing to maintain funding from both research councils and industrial sponsors, and a punishing schedule of travel to speak at other institutions and conferences, he always found time to talk to his students, helping to raise flagging morale here or giving chemical tips there. Overseas visitors received a copy of George Mikes' *How to be an Alien* to help them settle into the sometimes arcane Oxford world, and he never missed a group meeting.

During this period Malcolm's research interests began to diversify away from classical organometallic with increasing forays into solid state chemistry and heterogeneous catalysis. There was a successful spin-out company Oxford Catalysts (today Velocys) devoted to Fischer-Tropsch routes to sustainable fuels, and whose shares are traded on the AIM market. The discovery of buckminsterfullerene (C60) and then carbon nanotubes led to the conversion of the MVS machines into nanotube factories and an interest in finding ways to use the nanotubes like miniature test tubes. Malcolm and his students devised simple ways of opening the ends of the tubes using first nitric acid and later hot steam. When molten metals failed to fill the tube, they turned to salts. This proved a new and extremely fertile field where twisting ribbons of sodium chloride and other salts could be observed to be confined inside the tubes using electron microscopy. He also devoted a growing amount of his time to thinking about writing about his CBC bonding methods and related issues at the interface of theory and education.

Shortly after arriving in Oxford, Malcolm met Jennifer Bilham, who was a chemistry postgraduate student working with Jack Linnett and then Peter Atkins. They were married in 1965 and the reception was held in Balliol. Jenny, relaxed and down-to-earth where Malcolm was extrovert and dramatic, went on to become a distinguished academic in her own right, an outstanding theoretician who, in addition to her own interests, used spectroscopic and computational tools to unravel the detailed electronic structure of compounds, including some made in Malcolm's group. When answering subtle bonding questions at conferences, Malcolm would often reply, 'I think you'd better ask my wife about that.'

Alongside chemistry, Jenny and his children were the loves of his life. He was very proud of their three children, Sophie, Russell, and Matthew, who have all gone on to have successful careers, outside academia, let alone chemistry. In case it has not already become clear, Malcolm was a man of tremendous energy. In 1974 he and Jenny bought a derelict farm in Great Wolford in the Cotswolds which they spent the next decade restoring to its current magnificent state. Malcolm did a lot of this with his own hands at weekends, meticulously reconstructing the parquet floor in one room using wood recovered after flood damage in the ICL. Malcolm and Jenny were also

On Balliol Hall steps (front row, centre) with friends and colleagues at his 80th birthday celebration.

enthusiastically assisted by willing (we've checked!) graduate students who were rewarded for their efforts with beer and food at the local pub.

Malcolm Green left an indelible and unique imprint on inorganic chemistry. But equally important is his legacy in people. Over 100 of his students and collaborators have become academics; at least a third of these are in the UK. The same number have gone into industry and other walks of life. Rather than simply following directly in his footsteps many have veered into an extraordinarily broad and varied range of original topics, a sign of the can-do attitude that Malcolm instilled in everyone around him. On the occasion of his 80th birthday, a dinner at Balliol attracted almost 200 chemical friends and alumni from across the world. When the pandemic subsides, we suspect Malcolm would want us to gather again, to eat, drink and scrawl over beer mats and to let the ideas flow.