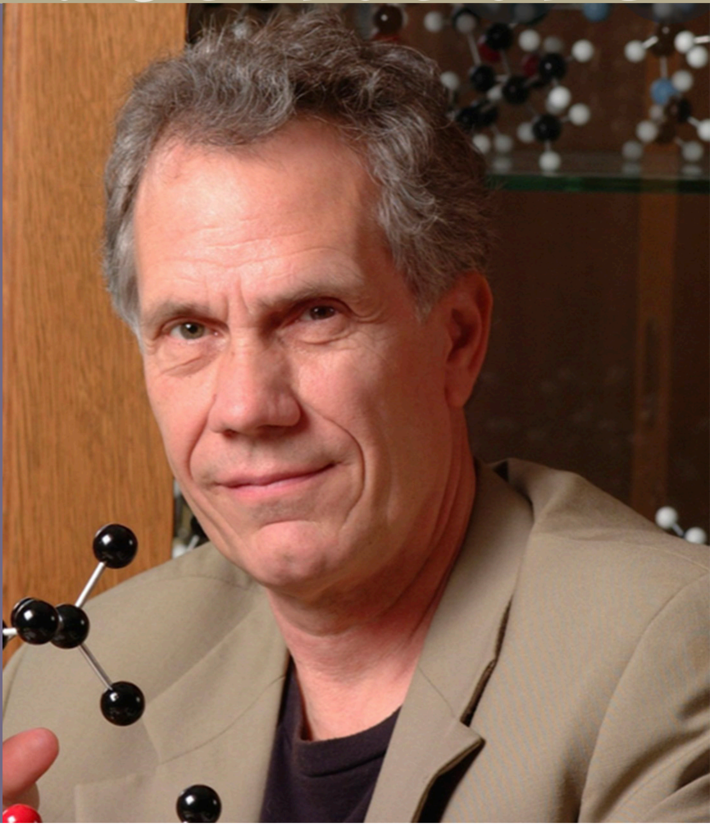
Malcolm H. Chisholm

1945–2015

BIOGRAPHICAL *Memoirs*



A Biographical Memoir by
Richard J. Puddephatt
and Robert H. Crabtree

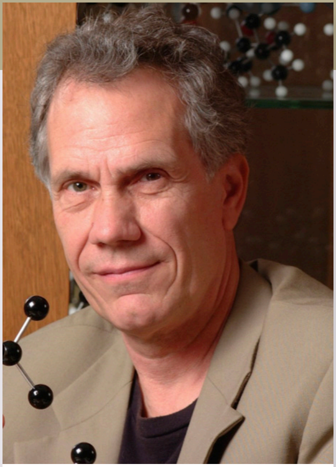
NATIONAL ACADEMY OF SCIENCES

MALCOLM HAROLD **CHISHOLM**

October 15, 1945–November 20, 2015

Elected to the NAS, 2005

Malcolm Chisholm, one of the most creative and distinguished inorganic chemists of his generation, was particularly renowned for his work on compounds containing metal-metal multiple bonds and their applications for catalysis and in functional materials. Very early in his independent career he reported the remarkable compounds $X_3M{\equiv}MX_3$, with M being molybdenum or tungsten and X being alkoxide or dialkylamide. He and his group then showed how they could activate organic compounds in unusual ways, often with changes in the metal-metal bond order. He was a master of synthetic chemistry, but he also made notable discoveries in theory, spectroscopy, and catalysis. Personally, he was highly outgoing, generous, friendly and fun-loving. He was also faithful and supportive of his family, students, colleagues, and his many friends around the globe and took great pleasure in their many successes.



By Richard J. Puddephatt and Robert H. Crabtree

Early Life and Interests

Malcolm was born in 1945 to Scottish parents, Angus and Gweneth Chisholm, in Bombay (now Mumbai), India. A career officer in the British army, Angus had been involved in military intelligence operations against Japan in Burma (now Myanmar), and Gweneth, a primary school teacher, was in India in connection with code-breaking operations. When Malcolm was six months old, the family moved back to their ancestral home in Inverness, Scotland, and then on to Dorset, in the south of England, when Malcolm was aged three. It was here that he spent his formative years, though a slight Scottish burr could always be detected in his speech and he always cherished his Scottish heritage. He remembers being captivated by science even at the young age of four: “My first interests in science were meteorological, trying to predict storms, rain, and when it would snow,” he said.[1] He then added: “Of course, that was frustrating because it doesn’t snow much in the south of England.” By the time he was nine, Malcolm’s interests had moved on to astronomy. With his telescope, he identified the moons of Jupiter and, in 1957, enjoyed viewing the naked-eye Arend-Rowland comet. Malcolm retained a strong amateur interest in both meteorology and astronomy and could often be found contemplating the sky for threatening clouds or interesting astronomical events.

In the late 1950s, Malcolm was given a chemistry set. In those days, one could buy many different chemicals from a standard pharmacy and, like many a schoolboy of that era, he was able to obtain materials in this way for a variety of private experiments. For example, he found that the combination of sodium chlorate and sugar was a suitable propellant for good homemade rockets. His experiments took place unfettered by his parents until a particular incident drew the local fire brigade: "I had a bit of a fire in the garden shed, [and] that was the end of my independent experiments." After that, he completed his school days safely,[1] with his mother Gweneth having a strong influence on his decision to go on to university.

Student Days at Queen Mary College, London, 1963–69

Malcolm entered Queen Mary College (QMC), London, in 1963, but his multiple interests in meteorology, astronomy, and chemistry made it difficult to choose just one subject for his degree. He briefly considered meteorology but noted, "I discovered you had to have a degree in math." So Malcolm settled on chemistry because, he said, "it was one of the subjects that came most easily to me" although he did not envision becoming a professional chemist at that time.[1]

Unsurprising in someone with such strong social gifts, Malcolm threw himself into the life of the university and became social director for the Students' Union. He spent much of his undergraduate years booking and promoting rock concerts by rising stars from the 1960s London music scene, such as Eric Clapton, The Yardbirds, The Animals, and The Who. Malcolm became known as "Big M," a moniker befitting his Mick Jagger style of dancing, his gold-tipped Black Russian cigarettes, and his sweet-talking entrepreneurial spirit. Malcolm graduated successfully with a bachelor of science in chemistry from QMC in 1966, an achievement that came as something of a shock to his professors, and even to himself, as he had come close to giving up school to pursue a career in music promotion. Although he never gave up his love of music and dancing, Malcolm now shifted his abundant energy to the world of science.[2]

A major turning point for Malcolm's career in chemistry occurred during his final undergraduate year, when he carried out a successful research project in the laboratory of a young lecturer named Alan Massey, who was later to become a distinguished professor of inorganic chemistry at Loughborough University. Malcolm found that when iron pentacarbonyl, $Fe(CO)_5$, in a sealed, evacuated Pyrex flask was exposed to sunlight (an experiment requiring careful timing in cloudy London) crystals of di-iron enneacarbonyl, $Fe_2(CO)_9$, were deposited on the walls of the flask. The binuclear iron carbonyl complex $Fe_2(CO)_9$ had been known for many years, but doubt had been cast on its authenticity based on its surprisingly low solubility and volatility for a covalent compound of such a low molecular weight. Malcolm showed that $Fe_2(CO)_9$ could be sublimed under high vacuum and that it gave a beautiful mass spectrum, which supported its proposed chemical formula. This undergraduate research earned him his first publication, a brief communication in *Nature*.[3] It was at this point that Malcolm found that he loved open-ended, curiosity-driven research and that he had a natural talent for synthetic chemistry, which made him begin to envisage a future career in chemistry.

Malcolm stayed at QMC for his Ph.D. studies and was initially planning to continue his research with Alan Massey. He eventually decided to work with Don Bradley, who had been appointed to the chair of the Inorganic Chemistry Department in 1965. Educated at Birkbeck College, London, Bradley stayed there as lecturer from 1949–59, before becoming professor of Inorganic Chemistry at the University of Western Ontario from 1959–65 in the Canadian London. Don had promised his wife that they would one day return to the United Kingdom, and research in England was attracting more government support in the 1960s than in the immediate post-war years, so he decided to move back and to take up the offer of a chair at QMC.[4] He had recently discovered that volatile molecular alkoxides of several transition metals could be obtained if bulky alkyl groups were used, so as to prevent oligomerisation through the formation of alkoxide bridges. These were very early examples of transition metal compounds with low coordination numbers with a fundamental importance that was quickly recognised by the growing community of inorganic chemists. Later, the volatile alkoxides became commercially important precursors for metal oxide materials by chemical vapor deposition (CVD) a field in which Don Bradley was also a pioneer. While in Canada, Bradley had begun to study the related dialkylamide complexes of transition metals, and he was keen to bring this interesting field of research with him to QMC. Malcolm joined this endeavor and made several key discoveries. The synthetic strategy was very simple and involved anion exchange reaction between a transition metal chloride and a lithium dialkylamide, according to Scheme 1, in which M is a transition metal and R is an alkyl group such as methyl, Me, or ethyl, Et.

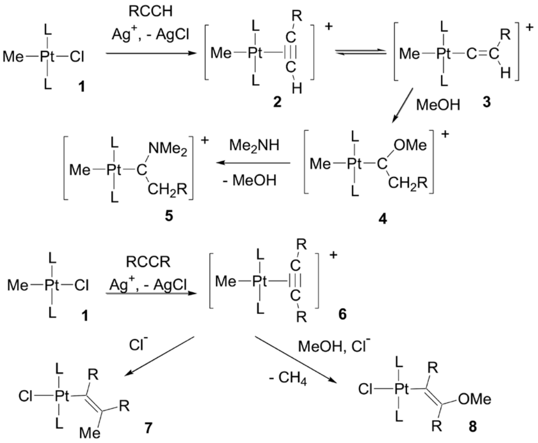
$$MCl_n + n\ LiNR_2 \longrightarrow M(NR_2)_n + n\ LiCl$$

The actual synthesis was difficult at that time, however, because most of the products were very easily hydrolysed or oxidised, and suitable equipment, such as the modern dry box normally needed for such sensitive compounds, was not yet widely available. Instead, the students used vacuum lines and special glassware, doing most of their own glass blowing. Similarly, characterisation of the new compounds was challenging. X-ray crystallography was very slow and by no means routine, and because most of the compounds were paramagnetic, the developing technique of NMR spectroscopy was not usually helpful. A further complication was that the reactions often took place with partial reduction of the transition metal compounds. For example, the molybdenum(V) chloride $MoCl_5$ gave the purple diamagnetic molybdenum(IV) dimethylamide, $Mo(NMe_2)_4$, and $NbCl_5$ gave paramagnetic $Nb(NEt_2)_4$. Chromium(III) chloride, $CrCl_3$, initially gave $Cr(NEt_2)_3$ but this disproportionated easily to chromium(II) and chromium(IV), and the volatile compound $Cr(NEt_2)_4$ was then obtained as a green, paramagnetic liquid. Malcolm was fascinated by their structures, colors, and magnetism, and he taught himself Ligand Field Theory to account for their unusual properties, the first of several forays he made into the world of theory. He developed some of the early bonding theories involved in π-donor complexes. For example, he could explain why a four-coordinate d^2 ion could be diamagnetic, as was the case for $Mo(NMe_2)_4$. He also found interesting reactivity of his new compounds, for example, $Cr(NEt_2)_4$ reacted easily with t-butanol to give the chromium(IV) *t*-butoxide $Cr(O\text{-}t\text{-}Bu)_4$ as a volatile blue solid.

A reaction between tungsten hexachloride and lithium dimethylamide intended to give tungsten hexa(dimethylamide), $W(NMe_2)_6$ initially seemed to go as planned. Malcolm took a flask containing his precious sample to a crystallographer, who promptly dropped it on the bench. Surprisingly, the expected rapid decomposition on exposure to moist air did not happen, and Malcolm just scraped up the sample, redissolved it, and re-used it. It turned out that steric crowding by the twelve methyl groups protected this compound from the normal easy hydrolysis of metal amides. Several years later, when Malcolm was at Princeton University, he found that his original sample of $W(NMe_2)_6$ had been formed as a mixture with the very novel and unexpected tungsten(III) compound, $W_2(NMe_2)_6$. The compounds had such similar solubility and volatility that they could not be separated during his Ph.D. work. At Princeton, however, he found that $W_2(NMe_2)_6$ could be hydrolysed by t-butanol to give $W_2(O\text{-}t\text{-}Bu)_6$, whereas $W(NMe_2)_6$ was inert. The resulting mixture of $W_2(O\text{-t-}Bu)_6$ and $W(NMe_2)_6$ could be separated, finally giving a pure sample of W(NMe$_2$)$_6$. Bradley and Malcolm later reviewed these early adventures in transition metal dialkylamide chemistry.[5] Malcolm considered his advisor, Don, as a key influence and a fine role model, both as a mentor and as a person. Of course, Malcolm was still a great socialiser, and amongst his many initiatives was to introduce group meetings at the local pub. Don noted that the level of excitement, both inside and outside the lab, decreased markedly after Malcolm graduated in 1969. The year before he graduated with his Ph.D., Malcolm married Susan Sage, who graduated with a bachelor of arts degree in English from QMC. Together in 1969, they moved to London, Ontario, for further studies.

Postdoctoral Research at the University of Western Ontario, 1969–72

After graduation, Malcolm and Sue moved to the University of Western Ontario (UWO) in London, Canada, where Malcolm took up a teaching postdoctoral fellowship and Sue enrolled in the Ph.D. program in English. Malcolm had arranged to do his postdoctoral research with Howard Clark, a New Zealander who had completed a second Ph.D. with Harry Emeleus at the University of Cambridge before taking up his first academic position at the University of British Columbia in Vancouver, Canada, in 1957. Coincidentally, Howard Clark had then replaced Don Bradley as professor of inorganic chemistry at UWO in 1965 and had also taken on the role as head of the chemistry department. By 1969, the Clark group was well established at UWO, and his main research theme was now in transition metal chemistry. In platinum chemistry, the discovery of the cationic carbonyl complex, $[PtCl(CO)(PR_3)_2]^+$, often known as "Clark's cation," was one of several notable achievements. Research in alkylplatinum chemistry had recently been initiated by postdoctoral fellows Dave Ruddick, who was already expert from his Ph.D. research in organoplatinum chemistry with Bernard Shaw, and by one of the present authors (RJP), who had completed his Ph.D. the previous year with Alwyn Davies and Robin Clark. Malcolm's project on the chemistry of cationic alkene and alkyne complexes of platinum, analogous to Clark's cation, advanced rapidly in his talented hands. He found this synthetic chemistry very easy compared to his prior metal amide chemistry and he made important discoveries very quickly, as shown in Scheme 2, which demonstrates some reactions of cationic alkyne complexes of platinum(II). R is an organic group (Me, Ph, CF_3, CO_2Me) and L is a neutral ligand (often PMe_2Ph or $AsMe_3$).



Although NMR spectroscopy was the main day-to-day tool for determining the structures of organoplatinum compounds, Malcolm was not accustomed to using this technique. For the first month or two, he would come by RJP's lab with his spectra to check his interpretation, but he soon became expert, and the roles were then often reversed. Later, Malcolm did some state-of-the-art research with Howard Clark and Jake Stothers on ^{13}C NMR of organoplatinum compounds, and he continued to use NMR spectroscopy creatively through his career. Shortly after Malcolm started at UWO, a young graduate student Leo Manzer and Australian postdoctoral fellow Trevor Appleton joined the group, along with Kenji Itoh (Nagoya University) and John Ward (University of British Columbia), all working on organoplatinum chemistry. This was a tremendous team, and, often working collaboratively, they spurred each other on to greater efforts. Leo went on to a distinguished career in industry at DuPont, later leading their efforts to develop environmentally benign aerosols and refrigerant gases, and Trevor continued to work with platinum compounds from a bioinorganic chemistry perspective during his academic career at the University of Queensland.

The most important concept to emerge from Malcolm's time at UWO was to see cationic complexes of platinum with alkenes and alkynes as metal-stabilised carbocations, a point of view that rationalized their high reactivity. The cations were generated by abstraction of a chloride ion from a neutral organoplatinum complex, such as step 1 in in the above examples, in the presence of an alkene or alkyne. Terminal alkynes gave the alkyne complex **2**, which could undergo a hydride shift to give an isomeric vinylidene complex **3**, as a reactive intermediate, that could then react with alcohols such as methanol to give stable alkylidene complexes such as **4**. Stronger nucleophiles, such as dimethylamine, could displace the methanol from **4** to give the new alkylidene complexes **5**. Internal alkynes gave the cationic complexes **6** and some of these could be isolated as stable compounds, but several underwent intramolecular insertion to give **7** or attack by external nucleophiles to give **8**. Both **7** and **8** are vinylplatinum complexes but with different stereochemistry. The concept of metal-stabilised carbocations has continued to be valuable for understanding both fundamental chemistry and applied catalysis. Similarly, the alkyne route to alkylidene complexes was a landmark discovery that has been exploited by many other research groups. Malcolm and Howard Clark published nineteen papers together, including an influential review article.[6] Malcolm valued his time at UWO and especially the mentorship and support from Howard Clark, a wise man who later provost of the University of Guelph and then president of Dalhousie University. Malcolm also benefitted greatly from the visits of distinguished professors who gave research lectures and interacted informally with department members, often taking in Malcolm's group meetings in the nearest pub. Malcolm recognized what it would take for him to join them at the top of the field and realised that he would have to substantially raise the level of his game, so he left UWO in 1972 determined to do so.

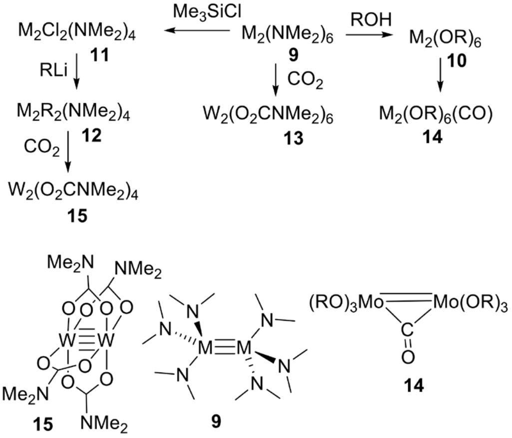
First Faculty Position: Princeton, 1972–78

Since there were few openings elsewhere in 1972, Malcolm broadened his horizons to include the United States by arranging a second postdoctoral position with Al Cotton at the Massachusetts Institute of Technology. Before he could start, however, he was offered a position as an assistant professor at Princeton. Malcolm decided to see Cotton personally to discuss the new situation, with the result that Cotton strongly advised him to take the Princeton appointment, thus beginning what became a very close friendship. In his Autobiography[7] Cotton refers to this as a "cherished friendship" that ultimately resulted in more than forty jointly written articles. Malcolm's future career was strongly influenced by this connection with Cotton, who was then the most influential inorganic chemist in the country. Cotton was also an expert on metal-metal bonding, a topic that Malcolm would develop collaboratively with him in the first part of his own career.

With their three rising stars, Princeton became a center of excellence for inorganic and organometallic chemistry in the 1970s. Along with Malcolm, there was Jeff Schwartz of hydrozirconation fame as well as Malcolm's regular opponent at squash, and Jack Norton, noted for his work on organometallic reaction mechanisms, osmium carbonyls, and metal hydrides.

In beginning his independent research, Malcolm was unsure whether to pursue his interest in organoplatinum chemistry or in metal amide and alkoxide chemistry, but the granting agencies made the decision for him, and he soon focused his efforts on the amides and alkoxides of molybdenum and tungsten in their lower oxidation states. Once he realized that his new compounds contained metal-metal bonds, it became clear that X-ray structure determination would be needed to make progress. Because Princeton did not have such a facility, Malcolm contacted his good friend Al Cotton, then at Texas A&M University, who had state-of-the-art X-ray equipment, plus a strong interest in metal-metal bonds and the expertise for working with air-sensitive compounds. Thus began a long and fruitful collaboration leading to continuing growth of their mutual friendship, in which Malcolm pursued the synthesis and reactivity of the compounds and Al Cotton looked after the X-ray structure determinations. They also applied their combined expertise in interpreting the structure and bonding properties. Malcolm and Cotton later exchanged a series of students both to enhance their collaboration and to give the students a wider perspective. For example, Malcolm's student Mike Extine went from Princeton to Texas A&M and Carlos Murillo graduated from the Cotton group to become Malcolm's first postdoctoral fellow and lifelong friend.[8]

The Chisholm group soon found that reaction of $MoCl_3$ with $LiNMe_2$ gave the key compound, $Mo_2(NMe_2)_6$ and that the reaction of WCl_4 with $LiNMe_2$ gave pure $W_2(NMe_2)_6$ free of the $W(NMe_2)_6$ contaminant that had plagued Malcolm's earlier studies at QMC. These new binuclear compounds were shown to contain metal-metal triple bonds and to have staggered conformations analogous to ethane, as expected for compounds with $\sigma^2\pi^4$ electron configurations and analogous to the bonding situation in acetylene. The first such compound, $W_2(CH_2SiMe_3)_6$, had already been reported a few years earlier by Nobel winner Geoffrey Wilkinson at Imperial College London, but its chemistry remained undeveloped. Malcolm quickly recognized that his compounds should have an extensive chemistry, resulting from the high reactivity of both the metal nitrogen bonds and the metal-metal triple bonds. For example, in the following diagram, dimethylamide groups in **9** could be substituted by reaction with bulky alcohols to give $M_2(OR)_6$, **10**, or with trimethylchlorosilane to give $M_2Cl_2(NMe_2)_4$, **11**. The chloride groups in **11** could then be replaced by alkyls to give $M_2R_2(NMe_2)_4$, **12**, and Malcolm showed that these unsymmetrical compounds **11** or **12** could exist as *anti* or *gauche* conformers. In other work, carbon dioxide inserted into some or all of the $M\text{-}NMe_2$ bonds to give carbamate complexes, such as $W_2(O_2CNMe_2)_6$, **13**. In many cases, these reactions took place with retention of the metal-metal triple bond, even though the coordination number at tungsten or molybdenum could vary between four and seven. In other cases, however, the metal-metal bond was directly affected, as in the reaction of $W_2Et_2(NMe_2)_4$ with CO_2 to give $W_2(O_2CNMe_2)_4$, **15**, having a metal-metal quadruple bond. Likewise, unsaturated reagents such as CO could add to give products, such as **14**, in which the metal-metal bond order either decreased or the bond was completely broken. A comparison of the reactivity of Malcolm's triply bonded compounds M_2X_6, having π-donor ligands, with that of the compound $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ lacking them, revealed interesting differences. For example, simple ligands L could add to M_2X_6 to give $M_2X_6L_2$ in which the triple bond is retained, but the corresponding adducts $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4L_2$ contain only a metal-metal single bond. The Chisholm-Cotton collaboration thus defined a new area of inorganic chemistry[9] by now covered in all the relevant textbooks. The very closeness of the collaboration may have hurt Malcolm's independent visibility in his department, however, leading to his decision to leave Princeton. Jack Norton also had to leave shortly afterward. The intensity and duration of Cotton's annoyed reaction to these events is clear from his autobiography[7] in which he describes himself as thinking, "to hell with a place that piles one stupid move on another." Malcolm took a different view: to acknowledge his gratitude to Princeton, he later endowed a scholarship there, the Malcolm H. Chisholm Thesis Award, for outstanding undergraduate senior achievement in inorganic chemistry, and always took time to personally congratulate the student so honored.



Scheme 3. Early chemistry of metal-metal multiple bonds and selected structures.

On the personal side, Malcolm found time to make new friends and to maintain contact with old ones. Leo Manzer worked at DuPont in Wilmington, Delaware, so the Chisholms and Manzers were often able to meet at weekends. Malcolm liked to entertain, and he and Sue warmly welcomed and supported new students and post-doctoral fellows at their home. A particular joy was the birth of their son Calum on May 11, 1973. Amongst all these activities, Sue found time to work on her thesis[10] and successfully graduated with her Ph.D. from UWO. Strains in the marriage, however, led to separation and later divorce, making for a very difficult and sad time for them both. Sue moved to the University of Texas at Austin, where she has had a successful academic career in teaching, scholarly activity, and service as director of the Center for Women's and Gender Studies. After the divorce, Malcolm began organizing his next career move.

Indiana University, 1978–2000

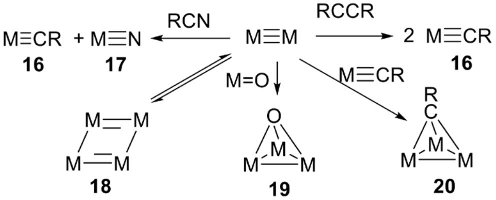
After considering a number of offers of faculty positions, Malcolm accepted one at Indiana University (IU), where he planned to continue his work on metal-metal bonds. Importantly, IU had an excellent X-ray structure service, with John Huffman in charge. The Chisholm-Cotton collaboration was therefore phased out, though their strong friendship continued. His colleagues at IU included Ken Caulton, with interest in inorganic and organometallic reactivity, and George Christou, working with molecular magnets. Together, they created a stimulating environment for inorganic research, often organizing symposia with students from neighboring universities. On May 1, 1982, Malcolm and Cynthia (Cyndy) Truax were married. At that time Cyndy was also Malcolm's secretary, and she was soon to take on the role of editorial assistant as Malcolm took on his first editorial position with the journal *Polyhedron*. Before long, in November 1983, Cyndy gave birth to twin boys, Derek and Selby, so a busy family life was guaranteed. The family liked to travel together, sometimes combining science and pleasure. On one occasion, Malcolm was visiting UWO while Cyndy took the twins to a local park, where the brake on the twins' stroller was somehow released and the stroller and twins rolled gently into the Thames River, with Cyndy in hot pursuit, fortunately with no harm done. Figure 1 shows the Chisholms on vacation, with a Loch Ness monster in the background. When at home, Malcolm and Cyndy were gracious and generous hosts and loved to entertain friends, colleagues, and students.

Figure 1: The Chisholms at Loch Ness. (Chisholm family photo.)

Figure 2: Malcolm with close friends Jack Lewis (left) and Al Cotton (right). (Chisholm family photo.)

Malcolm was in charge of the synthesis of margaritas at these events and, at their annual Christmas parties, his renowned Artillery Punch. Malcolm also owned a house in Cambridge, which he considered a second home, and where he went in the summers to escape the Midwest humidity, to relax, visit U.K. friends, and to catch up on writing projects. Al Cotton often passed through Cambridge on his summer trips, and they sometimes had the opportunity to meet up with their mutual close friend Jack Lewis,[11] (Figure 2) at that time arguably the most influential inorganic chemist in the UK. Malcolm even allowed Cotton to use his Cambridge house when on sabbatical in Cambridge.[7]

Towards the end of his time at Princeton, Malcolm had steered the emphasis of his research away from the synthesis of metal-metal triple bonded compounds to studies of their reactivity, and this was to become the main theme of his research throughout the 1980s. Their reactivity was limited in part by steric effects of the original dialkylamides and tertiary butoxides, so he moved to alkoxides with smaller alkyl groups, such as the isopropoxides. On the other hand, if the alkoxide groups were too small the compounds formed polymers, so Malcolm's trademark attention to detail was essential in finding the perfect Goldilocks systems. His research plan was to compare the properties of his triple bonds with those of alkynes. Both have $\sigma^2\pi^4$ electron configurations, but the d-orbitals in M_2X_6 allow a more diverse set of reactions. Addition reactions across the triple bond gave compounds with double or single bonds, as in similar reactions of alkynes. For example, reaction of $Mo_2(O\text{-}i\text{-}Pr)_6$ with di-isopropyl peroxide or bromine gave Mo=Mo double bonded $Mo_2(O\text{-}i\text{-}Pr)_8$ or Mo-Mo single bonded $Mo_2Br_4(O\text{-}i\text{-}Pr)_6$. Reactions with nitric oxide and pyridine completely cleaved the triple bond to give products such as $W(O\text{-}t\text{-}Bu)_3(NO)$(pyridine) from $W_2(O\text{-}t\text{-}Bu)_6$. There can be no analogy for this in organic chemistry, and some other reactions that differ from those of alkynes are shown, in simplified form, in Scheme 4.[12.13] Remarkably, carbon-carbon or carbon-nitrogen triple bonds could be broken to give carbyne complexes and nitride complexes. For example, $W_2(O\text{-}t\text{-}Bu)_6$ gives $W(CR)(O\text{-}t\text{-}Bu)_3$, **16**, and $W(N)(O\text{-}t\text{-}Bu)_3$, **17**. In some cases, the compounds could equilibrate with dimers, as in the reaction of $W_2(O\text{-}i\text{-}Pr)_6$ to give $W_4(O\text{-}i\text{-}Pr)_{12}$, **18**, or react with oxo or carbyne complexes to give $W_3(\mu3\text{-}O)(O\text{-}i\text{-}Pr)_9$, **19**, or $W_3(\mu_3\text{-}CR)(O\text{-}i\text{-}Pr)_9$, **20**, respectively. From a compound analogous to **14**, carbon monoxide could be reduced to carbide and oxide.



Scheme 4. Some unprecedented reactions of the metal-metal triple bonds in $M_2(OR)_6$ (M = Mo or W, alkoxide groups are omitted for clarity.)

To place the chemistry on a firm theoretical basis, Malcolm supported his student David Clark to work with Bruce Bursten, then a young assistant professor at Ohio State University (OSU). The collaboration was very successful, and Malcolm and David were awarded the American Chemical Society's (ACS) Nobel Laureate Signature Award on the basis of his superb Ph.D. thesis. Malcolm loved to celebrate the successes of his students, so this award gave him particular pleasure (Figure 3). This is but one example of how Malcolm enjoyed highlighting the accomplishments of his associates throughout his career, while also giving them abundant career advice. The beauty of the Chisholm chemistry with metal-metal multiple bonds was internationally recognized and attracted many other major awards from the ACS and Royal Society of Chemistry. He was delighted by his election as FRS in 1990, at the age of 44, and by the later award of the Davy Medal by the Royal Society.

Figure 3: Malcolm and his student David Clark with their spouses at the Nobel Signature Award ceremony. (Chisholm family photo.)

During his long stay at IU, Malcolm was developing an interest in materials chemistry, at first through a recognition that his metal alkoxides could act as models for reactions proposed to occur at the surface of metal oxides during bond activation and catalysis.[14-16] Later, in collaboration with his colleague Ken Caulton, Malcolm used his volatile tungsten compounds as precursors to tungsten carbide, tungsten nitride, or even tungsten metal. They also devised routes to volatile compounds of barium and copper and used them as precursors of materials such as barium oxide and metallic copper. Independently, Malcolm began to develop a major research project on the use of metal alkoxides for polymerisation of dilactides, oxiranes, and other ring compounds to create environmentally benign polymers from renewable resources. He also became intrigued with another new project based on the spectroscopy of compounds with metal-metal multiple bonds, with the idea of developing photonic materials. He considered but did not accept a number of attractive offers to relocate from Indiana during his stay there, but in 1999 he finally received an offer from OSU that he could not refuse. His friend and collaborator Bruce Bursten had risen through the ranks there and was chair of the Chemistry Department, where there were excellent facilities and expertise to support his growing interest in materials science. Their most generous offer also appealed to Cyndy in view of her Midwest roots.

The Ohio State University, 2000–15

In January 2000, Malcolm made what would be his final move from Bloomington, Indiana, to the Ohio State University as Distinguished Professor of Mathematical & Physical Sciences. The negotiations had been protracted, and the first indication that the offer had finally been accepted was when Malcolm phoned Bruce Bursten to invite him to visit the new Chisholm family home in Worthington, Ohio. Soon the research was again in full flow, stimulated by interactions and collaborations with new colleagues and, with his prodigious energy, continued unabated even as he served both as department chair from 2007-2011 and as associate director of Ohio State's Institute for Materials Research. He was involved in early planning for an award-winning new Chemical and Biomolecular Engineering and Chemistry Building, which opened in 2015. In 2006, he was named Distinguished University Professor, the highest honour at OSU. External awards were also showered upon him, including election as a member of the National Academy of Sciences in 2005 and as a Fellow of the American Academy of Arts and Sciences, of Die Deutsche Akademie der Naturforscher Leopoldina, and of the American Chemical Society. Warming his Scottish heart, he was also elected as Corresponding Fellow of the Royal Society of Edinburgh. One of Malcolm's idiosyncrasies was that he made permanent molecular models of his more interesting molecules, which he kept in a display cabinet in his office (Figure 4). He was much in demand as a seminar and conference speaker and would sometimes send a parcel of these models on ahead for dramatic effect in his lectures. A lifelong vegetarian on moral grounds, he continued to enjoy cigars, Scotch whisky, and Jaguar cars, to make new friends wherever he travelled, and to write with a fountain pen long after it became challenging to find either the pen or the ink.

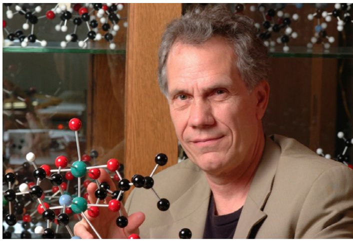
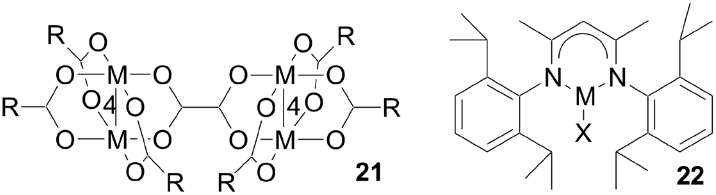


Figure 4: Malcolm at OSU with molecular models. (Photograph © National Academy of Sciences.)

At OSU, Malcolm switched his emphasis to “paddlewheel” compounds with quadruple metal-metal bonds having the $\sigma^2\pi^4\delta^2$ electronic configuration. Earlier, he had developed routes to these compounds, such as **15** (Scheme 3), by reductive elimination from compounds with triple bonds. Now he wanted to link two or more of these quadruply bonded centres to make dimers (such as the oxalate-bridged dimer **21** in Scheme 5), oligomers or polymers and even liquid crystals, by using either covalent linkers or supramolecular self-assembly, to produce interesting material properties. To probe the electronic properties of these new compounds, he used his own expertise in spectroscopy and theory and, in this interdisciplinary area of science, also collaborated with Robin Clark in resonance Raman spectroscopy, with his young IU colleague Jeff Zaleski in low temperature electronic spectroscopy, with his new colleagues at OSU Bruce Bursten and Christopher Hadad in theory, with Pat Woodward in structure determination, with Art Epstein in electroluminescence and EPR, and with Terry Gustafson and Claudia Turro in studies of excited states by ultrafast absorption and emission spectroscopy. During this period, he discovered intimate electronic fine structure, new charge-transfer excited states and developed a new understanding of the intervalence charge transfer in dinuclear units.[17-20]



Scheme 5. Oxalate-bridged dimer of quadruply bonded dimers, **21** (M = Mo or W, R = *t*-Bu) and a single-site catalyst for lactide polymerisation, **22** M = Mg or Zn, X = alkoxide, aryloxide or dialkylamide.)

Malcolm’s second major theme at OSU was in the general area of green chemistry, in particular in the synthesis of oxygen-containing, biodegradable polymers from sustainable sources. His main emphasis was on the polymerisation of dilactide, which is readily available from corn, to make polyesters, but he also worked on polymerisation of epoxides to polyethers and copolymerisation of epoxides with carbon dioxide to make polycarbonates. Most conventional catalysts for these processes were heterogeneous and not very selective. Malcolm’s contribution was to design well-defined single-site catalysts that were both immortal, so as to make living polymers, and stereoselective, so as to optimise the functional properties of the polymers. His most active catalysts were based on complexes of magnesium, calcium and zinc, with one alkoxide group and with a bulky anionic ligand to discourage the alkoxide from bridging, Compound **22** in Scheme 5, being one such successful catalyst design. He found that organotin alkoxides were less active as catalysts but made it easier to study of the mechanism of polymerisation. Applying his typically thorough approach, his studies of the mechanisms of polymerisation allowed him to optimise catalyst reactivity and selectivity.[21] For the first ten years or so of the Chisholm tenure at OSU, the family flourished. The twins became independent, and Malcolm and Cyndy made plans for more extensive travels. Malcolm's chemistry continued to excel, and he attracted more awards, such as the D.Sc., honoris causa, from UWO (Figure 5), where he had a last reunion with Howard Clark. Tragedy was soon to strike, however, when both Malcolm and Cyndy became ill. Cyndy passed away in August 2012, leaving Malcolm bereft, but he took solace in his family, happily welcoming his first granddaughter, Fleur, in November 2012. Malcolm himself had been diagnosed with cancer and, for the last five years or so of his life underwent regular chemotherapy sessions, which he suffered bravely and cheerfully. He grew a beard, refused to quit, and continued with his teaching, research, and social life until very near the end. This includes throwing an "8-to-8" party for Christmas 2013, where he invited his whole group, family, and friends over to party and where he danced through the night. Still traveling extensively, and usually first class, he took memorable tours of Scotland in 2013 with Calum, Erica, and Fleur and in 2014 with old friends Cliff and Pam Kubiak and George and Kim Christou (Figure 6). He also treated himself to a new Jaguar sports coupe that year (his 510 hp "touring" Jag) to encourage him to take road trips to see old friends, often with his canine companion Butters (Figure 7). The end came on November 20, 2015, when he passed away peacefully at home at age 70 in the arms of his son Selby. He is survived by his sons Calum (daughter-in-law Erica and granddaughters Fleur and Soleil),

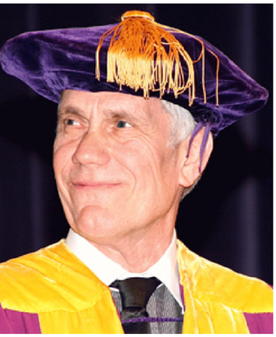


Figure 5: Malcolm at the UWO D.Sc. award ceremony. (Chisholm family photo.)

Figure 6: Malcolm (left) **with his good friends, Cliff Kubiak** (center) **and George Christou** (right). (Chisholm family photo.)

Selby (daughter-in-law Soobin and granddaughter, Oona), and Derek (daughter-in-law Lauren). A day or two before the end, Calum asked if he was frightened, to which he replied "Oh, not at all. I have had a wonderful life," thanks to all the friends and family who had given him so many happy memories.

Figure 7: Malcolm in his Jag.
(Chisholm family photo.)

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