New Developments in Making Compounds and Materials by Condensing Gaseous High-temperature Species at Atmospheric or Low Pressure

Peter L. Timms
School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

1 Introduction

It is well known that the use of high temperatures permits the formation of a wide range of gaseous atomic and molecular chemical species which are often unobtainable by other means. Many of these species such as the free atoms of the metals or low oxidation state oxides and halides of Group 13 and 14 elements have the potential both thermodynamically and kinetically to be chemically very reactive. As soon as the temperature is lowered the species become metastable and tend to recombine to form the less reactive gaseous or solid elements or compounds from which they were made. This recombination can be very rapid and often special conditions have to be established to make use of the species while they are still reactive.

Deriving useful chemistry from such species began to be a lively area of research in the 1960s following work by Skell on carbon vapour chemistry.[1] There was a frenzy of activity in the 1970s following the first work on transition metal atom chemistry at Bristol.[2–5] Developments have continued to the present but undoubtedly the biggest surprise in the 1980s and early 1990s again involved carbon in the synthesis of fullerenes, the remarkable molecular allotropic forms of that element.[6]

Section 2 below, the first main part of this review, surveys some experimental considerations relevant to using high-temperature species in synthesis, while the other three parts are concerned with work over the past few years at Bristol in exploiting the chemistry of neutral atoms and small molecules: Section 3 on reactions of metal atoms with hexafluorobenzene, Section 4 on microfibres formed by condensing silicon monoxide and Section 5 on some new silylene chemistry.

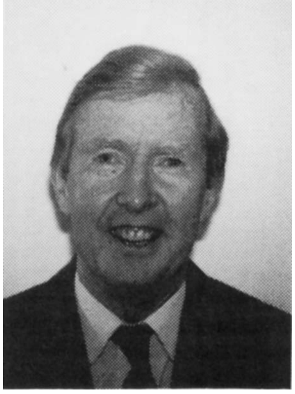
2 Experimental Conditions

High temperatures can be attained by many different methods including electrical resistance heating, flame heating, electron bombardment, focussed light beams, electric arcs and plasmas, and a detailed discussion of them is beyond the scope of this review. However, one point is worth making. If gaseous species are produced in thermal equilibrium with a heated solid or liquid, it is usually fairly easy to measure the temperature at which the species are formed and to predict the position of chemical equilibria. When species are formed under more dynamic conditions in flames, by laser pulses, in electric arcs or in plasmas or discharges, it is more difficult to define the temperature or know the position of chemical equilibria. In addition, high-voltage electrical discharges and plasmas will contain energetic electrons and ions. So the formation of species under dynamic conditions can create problems for the synthetic chemist which should not be underestimated. That said, dynamic methods may sometimes be the only way of generating species under particular conditions and they are being used successfully. To give three examples: working in the vacuum chamber of a Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectrometer allows ion–molecule reactions involving metal atoms or ions to be studied to great advantage,[7] rapid cooling-by-expansion of the vapour plumes created by a pulsed laser impact on carbon and metals allows many novel gaseous clusters to be made,[8] and arc and plasma evaporation techniques are responsible for much of the spate of fascinating new work on condensing 'nanotubes' of carbon, boron and other materials.[9]

Whatever method of generating the species is used, pressure is of crucial importance as it affects the ease of forming, condensing or reacting species. Figure 1 summarises how different pressure regions permit different types of chemistry involving high-temperature species to be carried out. Considering the situation at atmospheric pressure (10^5 Pa) first; if a metal is heated in a system containing an inert gas at 10^5 Pa, then rapid evaporation of the metal to form atoms will only be observed at a temperature when its vapour pressure is close to 10^5 Pa. The mean free path of the atoms formed will be very short so that as soon as the temperature of the gas falls, multi-body collisions of the gaseous atoms leading to nucleation of solid or liquid metal will occur. If an attempt is made to react the gaseous atoms with a gaseous substance, the substance and any reaction products will become heated by conduction from the surrounding hot gas and they will only survive if they are thermally stable. These effects impose severe limitations on the subtlety of the chemistry that can be carried out. Nevertheless, as it is easier to work at atmospheric pressure than in any other pressure region, a huge amount of work has been carried out on atmospheric-pressure processes involving high-temperature species generated from furnaces under thermal equilibrium conditions or under non-equilibrium conditions in flames, arcs or plasmas. In some cases interesting aggregation effects occur after nucleation of solids which can lead to useful materials (see Figure 1 and Section 4) and in other cases the high activation energy for nucleation permits alternative gas-phase processes to occur in preference: *e.g.* in a high-temperature synthesis of ethyne from methane in which the gas phase process $2CH_4 \rightarrow C_2H_2 + 3H_2$ occurs much faster at 2000 °C than the thermodynamically favoured $CH_4 \rightarrow C(solid) + 2H_2$.

Reducing the pressure below atmospheric has important effects on the position of chemical equilibria, on the frequency of collisions of gas molecules with each other and on the mode of condensation. For example, pressures just below atmospheric are being used in arc syntheses of the 'nanotubes' mentioned above.[9] Slightly lower pressures have proved to be the best for forming fullerenes. When carbon is evaporated under helium at 15 000 Pa the condensation of carbon vapour which occurs gives C_{60}, C_{70} and other cage forms of carbon. These molecules were first synthesised by pulsed laser evaporation of carbon in helium but it is now recognised that they can be formed by thermal or arc evaporation of carbon or even by controlled combustion of aromatic molecules.[5,6] The success of this chemistry owes much to the thermal stability of the carbon–carbon

After graduating from the University of Oxford in 1959, Peter Timms worked for Borax Consolidated and developed an interest in high temperature chemistry. This theme then shaped his D.Phil. research at Oxford (with C.S.G. Phillips), his postdoctoral research at Rice University (with J. L. Margave), and his research as Assistant Professor at Berkeley. He returned from the USA as a Ramsay Fellow at Bristol, later becoming Lecturer and Reader in Inorganic Chemistry. He was awarded a Corday Morgan Medal for work on synthetic reactions of boron, silicon and transition metal high temperature species. His current research, in addition to the topics of the review, include work relevant to the electronics industry on silica films and on destruction of toxic waste gases.



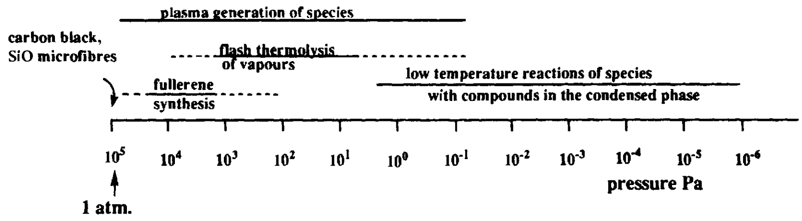


Figure 1 The pressure used for different types of synthesis involving gaseous high-temperature species.

bonds in the gaseous intermediates and in the final condensed product as molecules can only exist at high temperatures if they contain strong chemical bonds.

The pressure range of 10—1000 Pa has long found uses in flash vacuum pyrolysis of organic compounds, in which a compound is passed quickly through a heated tube and yields highly reactive fragments which can be used in synthesis. In this pressure range, there is still fairly efficient heat transfer from the hot walls of the tube to the gas so that reactive species are generated by energetic intermolecular collisions and then pass out of the hot zone rapidly because of the low pressure.[10]

When high-temperature species are generated at pressures below 0.1 Pa, individual atoms or molecules will travel many centimetres before their progress is seriously impeded by collisions with surrounding gas. Nucleation of solids from gases takes place slowly and may not be observed in ordinary vacuum systems in which collisions of species with the walls occur long before gas-phase nucleation. This makes it possible, for example, to transfer metal atoms efficiently from a hot zone where they are made through the vacuum to a cooler surface where they can be condensed; this is the principle behind the industrial method of vacuum metallization. These low pressures will also further facilitate formation of high-temperature molecular species from solid–solid or gas–solid equilibrium reactions. If the condensing surface is made sufficiently cold, it is possible to condense on it not just the gaseous high-temperature species but also the vapour of any compound which may react with the high-temperature species. Contact between the hot source of gaseous species and the added vapour can be made negligible so that even the most delicate molecules can be reacted with high-temperature species under these conditions. Cocondensation of high-temperature species with compounds on surfaces cooled in the range −100 to −269 °C is a valuable synthetic method which has been applied widely.[5] The very lowest temperatures are required if permanent gases like CO or N_2 are to be reacted with metal atoms and other high-temperature species and such work has usually been carried out on a milligram scale using *in situ* spectroscopic characterisation of products.[11] A great deal of work has used liquid nitrogen-cooled surfaces at −196 °C (as we have used for the work on hexafluorobenzene described in Section 3) and has been conducted on a scale ranging from milligrams to tens of grams of reactants. Species may also be condensed under vacuum into liquids of low vapour pressure. Commonly the liquid is a solution of a reactive compound in an inert solvent, cooled until it has a low vapour pressure (as we have used for silylene chemistry described in Section 5) but in some cases the pure liquid is the reactant.[12]

3 Reactions of Atoms with Highly Fluorinated Arene Ligands

Since the first work on transition metal atom chemistry at pressures <0.1 Pa,[2] one of the most successful uses of transition metal atoms in chemical synthesis has been the reaction of atoms with arenes to form bisarenemetal 'sandwich' compounds and related products with coordinated arenes. Hundreds of compounds have been made this way which are inaccessible or difficult of access by the conventional methods of organometallic chemistry involving reduction of metal compounds in the presence of arene ligands or ligand displacement reactions.[5,13–16] The sandwich compounds have been made with Group 3–8 elements with the largest number in Group 6 where the products are 18-electron complexes (six electrons from the metal and six π-electrons from each arene ligand) with greater stability than for comparable products from other Groups. However, by using bulky arene ligands like 1,3,5-tri(*tert*-butyl)benzene to provide steric protection, surprisingly stable complexes have been made of many early transition metals including 15-electron complexes of some of the lanthanide elements.[17,18]

We have been re-exploring this area using hexafluorobenzene and other highly fluorinated aromatic compounds as ligands. Relative to benzene or alkyl substituted benzenes, the electron withdrawing fluorine atoms reduce the availability of the aromatic π-electrons for σ-bonding to metals but enhance π-acceptor properties. Early work on condensing chromium atoms with hexafluorobenzene at −196 °C showed that no product that was stable at room temperature was formed but if benzene or trifluorophosphine was mixed with the hexafluorobenzene the stable compounds $[Cr(C_6F_6)(PF_3)_3]$ or $[Cr(C_6H_6)(C_6F_6)]$ could be isolated.[19] More recently, we have found that condensing molybdenum or tungsten atoms with hexafluorobenzene on a liquid nitrogen-cooled surface gives low yields (*ca.* 2% based on the metal atoms used) of $[M(C_6F_6)_2]$ (M=Mo or W) as quite volatile, air-stable, brightly coloured crystalline solids.[20] The compounds were best formed in the apparatus of Figure 2 in which the tip of an uncooled rod of Mo or W was heated by a focussed electron beam allowing rapid evaporation from a pendant drop of molten metal held by surface tension. The bisarene complexes are the only molecular products of the atom reactions apart from a trace of decafluorobiphenyl, so they are easily isolated on warming the condensate by first pumping away the excess hexafluorobenzene then pumping them or dissolving them out of the involatile/insoluble metal-rich residue on the condensation surface. Their air stability contrasts sharply with the behaviour of bisarenemolybdenum or tungsten compounds with less electron withdrawing ligands – some bisarenemolybdenum

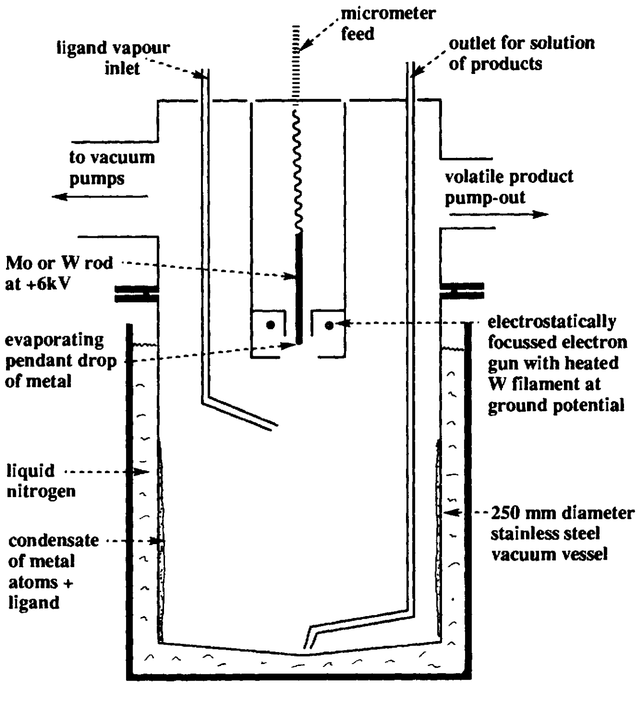


Figure 2 Apparatus used for efficient evaporation of molybdenum or tungsten by electron bombardment.

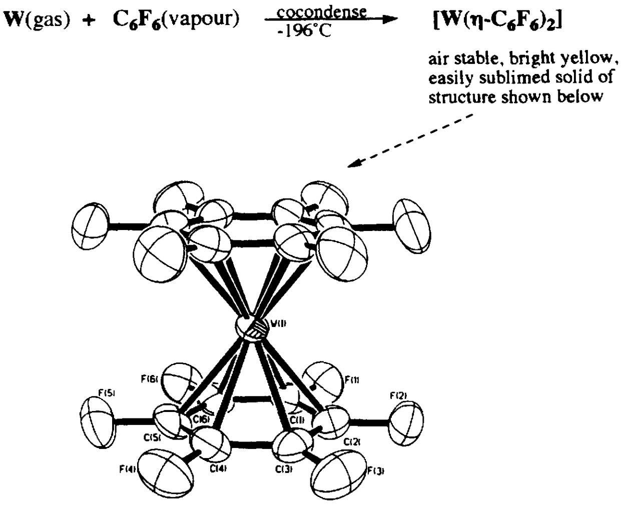


Figure 3 Preparation and structure of bis(hexafluorobenzene)tungsten.

compounds even catch fire spontaneously in air. The hexafluorobenzene raises the effective oxidation state of the Mo or W to a point where air oxidation cannot easily occur. Bis(hexafluorobenzene)tungsten decomposes at about 180 °C in either argon or in air showing its indifference to the presence of oxygen. The structure of $[W(C_6F_6)_2]$ (see Figure 3) determined by X-ray diffraction has tungsten–carbon bond lengths very similar to those in $[W(C_6H_5Me)_2]$ showing that the different σ-donor and π-acceptor properties of hexafluorobenzene and toluene must balance out.

Using mixtures of C_6F_6 and C_6H_6 or C_6F_6 and $C_6H_3F_3$-1,3,5 with Mo and W atoms gives the mixed products $[M(C_6F_6)(C_6H_6)]$ and $[M(C_6F_6)(C_6H_3F_3)]$ which show beautiful NMR spectra as the nuclei in the two rings couple to each other. This coupling produces well resolved septets in both the ^1H and ^{19}F NMR of $[M(C_6F_6)(C_6H_6)]$. For $[M(C_6F_6)(C_6H_3F_3\text{-}1,3,5)]$, the ^{19}F NMR (see Figure 4) shows a septet of quartets for the $C_6H_3F_3$ ring and a symmetrical 10-line multiplet for the C_6F_6 ring formed by a superimposed quartet of quartets in which the inter-ring F–F coupling constant is twice the inter-ring H–F coupling constant.

Atoms of the Group 8 metals ruthenium and osmium condensed with C_6F_6 have not yielded any stable complex $[M(C_6F_6)_2]$. With these metals, mixtures of non-halogenated arenes and hexafluorobenzene give products of type $[M(\eta^6\text{-arene})(\eta^4\text{-}C_6F_6)]$ in which the η^4-C_6F_6 ring is non-planar, *i.e.* the metal atom optimises its share of electrons from full coordination of benzene or an alkylbenzene and partial coordination of the poorer donor hexafluorobenzene.[21] We have made a compound $[Ru(C_6F_6)(PF_3)_2]$ from Ru atoms, C_6F_6 and PF_3 in which the hexafluobenzene appears to be η^6-coordinated but the complex decomposes at low temperatures and complete characterisation has proved very difficult.

Experiments with hexafluorobenzene and metal atoms have enabled us to explain better the way in which all low-temperature reactions between metal atoms and arenes occur.[22] Earlier work had shown that condensation of chromium or molybdenum atom with pure bromobenzene or with mixtures of benzene and bromobenzene gave no molecular product containing coordinated bromobenzene. Instead, oxidation of the metals by the bromobenzene occurred. We observed that condensation of the same metal atoms with a mixture of hexafluorobenzene and bromobenzene gave $[Cr(C_6F_6)(C_6H_5Br)]$ and $[Mo(C_6F_6)(C_6H_5Br)]$ respectively. How had the hexafluorobenzene permitted bromobenzene to coordinate to the metals without oxidising them? From this and many related experiments we found that the key is the sequence of addition of arene ligands to the metal atoms and the sensitivity to oxidation of the intermediate 'half-sandwich' complex.

At the very low temperatures at which metal atom reactions are conducted, only reactions with very low activation energies can proceed rapidly. When a chromium atom interacts with a bromobenzene molecule at low temperatures, two types of reactions are possible: complexation of the π-electrons of the bromobenzene to the chromium to give the half-sandwich $[Cr(C_6H_5Br)]$ or oxidative addition of bromobenzene to chromium to give C_6H_5CrBr. The evidence is that half-sandwich formation is the dominant process in this and all reactions of metal atoms with arenes. However, the chromium in the half-sandwich complex is more electron rich than a free chromium atom so it is more susceptible to oxidation and it is also harder for a second arene molecule to coordinate to it. Thus, bromobenzene rapidly oxidatively adds to $[Cr(C_6H_5Br)]$ forming chromium(II) products from which the coordinated arene is lost and $[Cr(C_6H_5Br)_2]$ is not produced. In the situation in which a mixture of C_6H_6 and C_6H_5Br is condensed with chromium atoms, the C_6H_5Br destructively oxidises $[Cr(C_6H_6)]$ as well as $[Cr(C_6H_5Br)]$, but with the $C_6F_6+C_6H_5Br$ mixture and chromium, $[Cr(C_6F_6)]$ is resistant to oxidation by C_6H_5Br and coordination occurs instead to give the observed $[Cr(C_6F_6)(C_6H_5Br)]$. These ideas are summarised in Figure 5.

Spectroscopic evidence for $[V(C_6F_6)]$ analogous to $[Cr(C_6F_6)]$ was obtained by Ozin[23] from EPR studies of the vanadium atom–C_6F_6 reaction under matrix-isolation conditions and we have recently made various complexes of type $V(C_6F_6)(\text{arene})$ on a preparative scale. However, neither $[Cr(C_6F_6)]$ nor $[V(C_6F_6)]$ seems capable of adding another C_6F_6 molecule to form the bisarenemetal

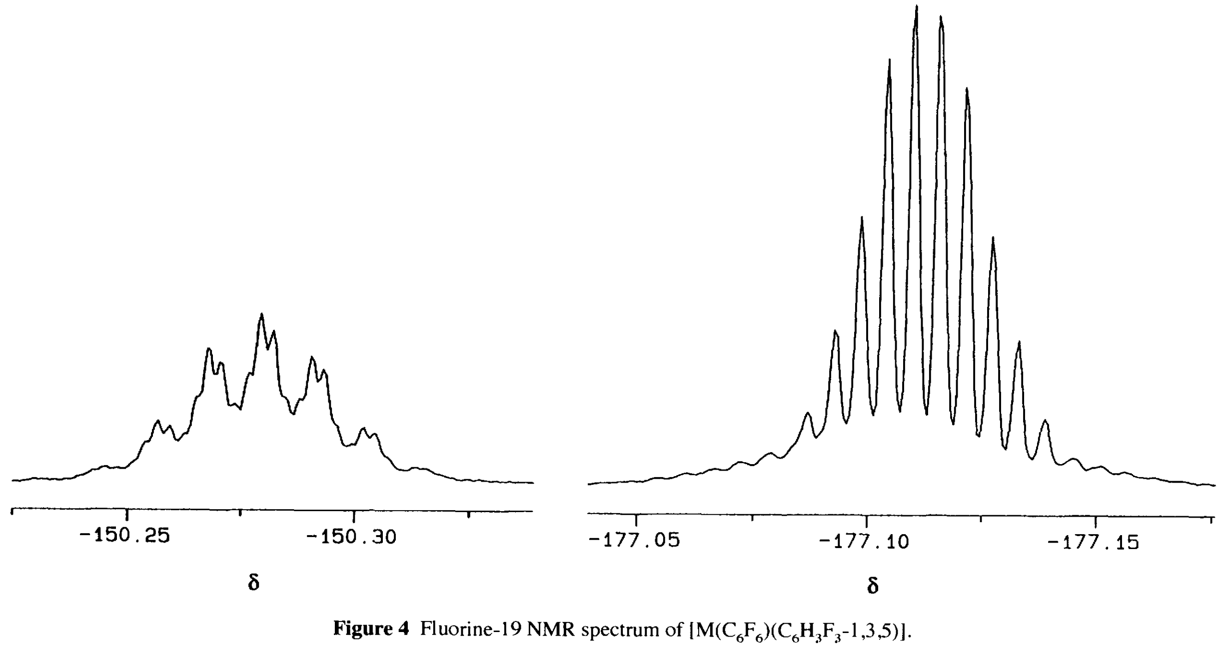


Figure 4 Fluorine-19 NMR spectrum of $[M(C_6F_6)(C_6H_3F_3\text{-}1,3,5)]$.

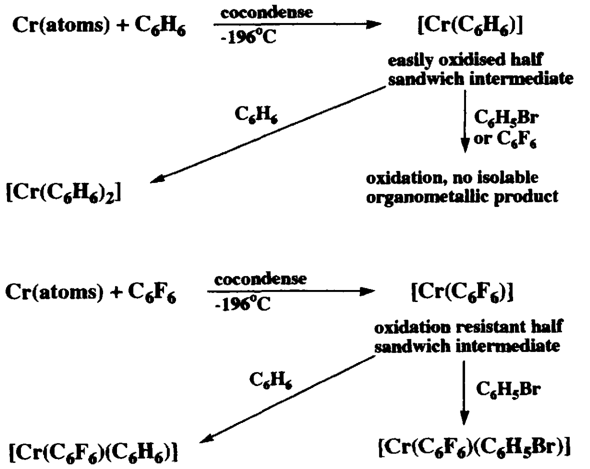


Figure 5 Comparison of redox properties of different half-sandwich intermediates in the reaction of chromium atoms with arenes.

complex although Mo and W can, presumably because the bonding capabilities of 3d orbitals are more strongly affected by an increase in effective oxidation state of the metal than are the 4d or 5d electrons of Mo or W.

Hexafluorobenzene is itself capable of destructively oxidising some half-sandwich molecules. In the reaction of molybdenum atoms with a mixture of C_6H_6 and C_6F_6, $[Mo(C_6F_6)(C_6H_6)]$ is virtually the only molecular product because any $[Mo(\eta\text{-}C_6H_6)]$ formed is destructively oxidised by C_6F_6 and the $[Mo(\eta^6\text{-}C_6F_6)]$ half-sandwich adds benzene much more easily than it adds hexafluorobenzene. This combination of the oxidising power and weak donor ability of C_6F_6 limits the range of metal atoms which will form stable complexes with hexafluorobenzene. For example, we have so far failed to make hexafluorobenzene complexes containing Nb, Mn, Re or Fe. However, these properties of hexafluorobenzene also complicate alternative approaches to studying its coordination chemistry without using metal atoms. Some progress has been made in this area[24] but it is likely that metal atom chemistry will remain the best approach for many of these products.

4 Condensation of SiO at High Temperatures – a Versatile Fibre-forming System

The molecule SiO is well known as a gas-phase species at high temperatures. In Norway and other countries rich in hydroelectric power, arc furnaces are used to produce metallurgical grade silicon and ferrosilicon from SiO_2/C and $SiO_2/Fe_2O_3/C$ on a huge scale. In these furnaces, the formation and reactions of gaseous SiO play a major part in reduction and heat transfer. Escape of hot gaseous SiO from the furnaces into the atmosphere leads to its oxidation and condensation as finely divided silica, SiO_2. This material used to be the main component of smoke effluents from such industrial arc furnaces which caused considerable damage to the local environment. After legislation forced the polluters to collect the silica instead of releasing it, they began seeking uses for the waste product. Today that collected silica is in such great demand as an additive for strengthening concrete that some arc furnaces are being run with the primary purpose of producing SiO_2 from oxidised SiO rather than silicon or ferrosilicon!

When hot gaseous SiO condenses in an inert gas stream, it forms a brown powder originally named nearly ninety years ago as 'Monox'.[25] This solid is basically a mixture of silicon and silica because there is no stable solid phase SiO and the disproportionation:

$$2SiO(gas) \rightarrow Si(liquid\ or\ solid) + SiO_2\ (viscous\ liquid\ or\ solid)$$

accompanies condensation. In the 1950s, the B. F. Goodrich Company in the USA undertook a study of the generation and condensation of SiO with a view to making solids of use as fillers for rubber. They reported in patents that if condensation is carried out from a smoothly flowing gas stream containing SiO plus an inert gas (CO, N_2 or Ar), the SiO condensed mainly in the form of microfibres and that the proportion of fibres could be increased by adding a low percentage of ammonia to the inert gas.[26]

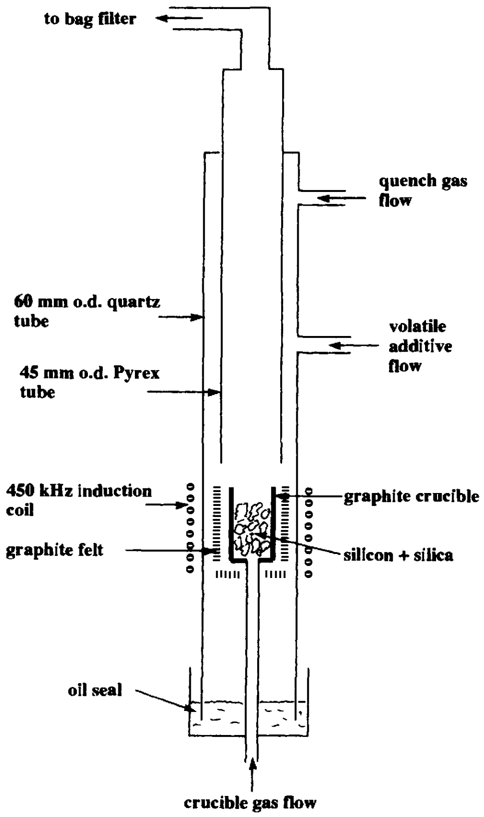


Figure 6 Apparatus for preparing and condensing gaseous SiO.

We followed up this work with the objective of learning more about the conditions under which fibres form but have also discovered that the morphology of the fibres can be changed by chemical additives.[27] Using the type of apparatus shown in Figure 6 we prepare SiO gas from a mixture of silicon and silica heated inductively in a graphite crucible to about 1800 °C. The SiO is carried upwards away from the crucible in a non-turbulent stream of N_2 or Ar and, as the gas stream cools, the SiO condenses to a brown solid which is collected in a filter. By scanning electron microscopy (SEM) the solid appears as groups of bent microfibres, of diameter around 20 nm and length of 200—300 nm as shown in Figure 7(a). Closer analysis by transmission electron microscopy (TEM) and powder XRD shows the silicon is present as microcrystallites. These are at highest concentration at the head but they also appear along the length of each fibre. The accompanying silica is amorphous. The surface area of the fibres is quite high, around 150 $m^2\ g^{-1}$. Conventional chemical analysis of the collected fibrous solid gives the composition as Si_4O_5, but if air exposure is rigorously avoided before analysis then we have proved that the composition is very close to SiO.[28]

Fibre growth occurs rapidly. We estimate that the time interval between nucleation of gaseous SiO and completed growth of the microfibres in the rising, cooling gas stream is <0.1 s. As noted in the B. F. Goodrich patents, the growth process is sensitive to a variety of physical parameters and we find that the condensed SiO consists of discrete fibres only if: (a) the gas stream leaving the crucible contains at least 10% SiO corresponding to the equilibrium pressure of SiO over SiO_2/Si at 1600 °C or above; (b) the gas flow is non-turbulent in the condensation region; and (c) the gas stream is fast enough to carry growing fibres rapidly away from the SiO source. Based on these observations, our proposals on the stages of fibre growth which occur in the apparatus of Figure 6 are as follows. The SiO vapour, mixed with inert gas, leaves the graphite crucible where it is formed and begins to cool by radiative heat loss;

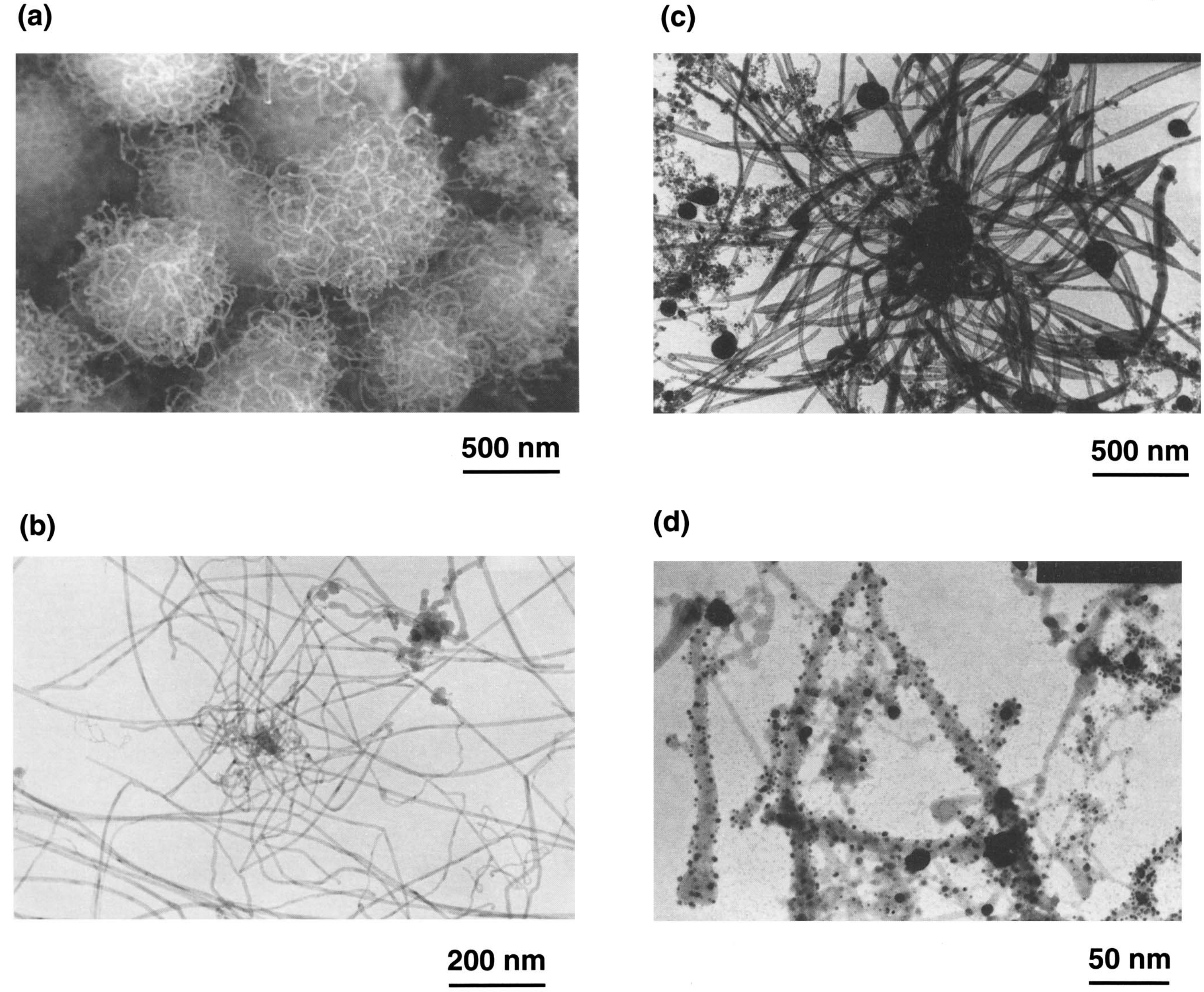


Figure 7 Electron micrographs: (a) SEM of fibrous condensed SiO; (b) TEM of SiO condensed in the presence of $AlCl_3$ vapour; (c) TEM of mixed condensate of SiO and GeO; (d) TEM of SiO condensed in the presence of WCl_6 vapour.

additional cooling is caused subsequently as the gases rising from the crucible mix with the cooler quench gas flow. At a distance of about 15 mm above the crucible and at a temperature estimated to be >1400 °C, the vapour becomes supersaturated and nucleation begins creating tiny, hot particles (studies have been made of SiO nucleation at sub-atmospheric pressure but not under conditions in which fibres would form[29]). The concentration of molecular SiO in the gas phase then drops very rapidly to a level at which it contributes little to further condensate development. As SiO is not stable in the condensed phase, disproportionation to liquid Si and viscous solid SiO_2 takes place within the tiny particles; these phases tend to segregate to give molten silicon and viscous silica-rich domains. Aggregation of the primary particles proceeds rapidly with a slight gain in enthalpy; the most favoured mode of aggregation will be for the molten silicon-rich areas on two particles to stick and coalesce followed by coalescence of the silica as it flows across the silicon surface. Repetition of this mode of aggregation gives the observed strongly asymmetric growth with a molten silicon-rich growth tip moving away from the solidifying silica-rich fibre tail. Segregation of silicon and silica is imperfect and some of the silicon is left imbedded in the silica in the tail. Growth of a fibre diminishes and eventually ceases as the supply of molten particulates is used up and as its own growing-tip head solidifies. Probably after solidification but while the fibres are still very hot, head–head collisions between fibres may cause sticking and the development of the cauliflower-like fibre groups visible in Figure 7(a). If the gas flow is turbulent, particulates in different stages of growth are intermixed and the progression of fibre growth is impaired. Unless the partial pressure of SiO vapour leaving the crucible is quite high, initially formed droplets do not grow fast enough to maintain themselves liquid and they eventually coalesce to give particulate material which appears to be made of loose aggregates of small spheres and sometimes poorly formed microfibres.

We have added a wide range of gaseous inorganic compounds to the gas stream carrying the SiO to find the effect on SiO condensation and fibre growth. Some of these are chlorides added as gases or vapours to the quench gas stream, *e.g.* $AlCl_3$, $GeCl_4$ or WCl_6 vapour. In these cases, the collected products are heated under vacuum to remove any condensed or adsorbed metal halides and then any remaining metal is present in the product as free metal or as an oxide. Other gaseous inorganic compounds are generated as high-temperature species along with the SiO from within the crucible mainly by adding oxides to the Si/SiO_2 mixture. For example, partial replacement of SiO_2 in the crucible by Ga_2O_3, GeO_2 or Li_2SiO_3 yields Ga_2O, GeO or Li atoms to be condensed together with the SiO.

Particularly striking changes in fibre morphology are obtained when the quench gas stream contains about 4% $AlCl_3$ vapour. The product then has much longer and less bent fibres than from SiO alone with less clearly defined head regions [Figure 7(b)]. Free silicon is still present in the fibres but very little of this is crystalline. There is *ca.* 5% of aluminium present as oxide in a non-crystalline mixed phase with silica Long fibres are also seen when Ga_2O_3 or GeO_2 is added to the Si/SiO_2 mixture in the crucible to form Ga_2O or GeO+SiO in the gas phase Fibres containing 20% Ge as GeO_2 are ribbon-like [Figure 7(c)] We have recently made very long microfibres by condensing SiO in the presence of lithium to give fibres containing a glassy SiO_2/Li_2SiO_3 phase and a Si phase which also contains some lithium [28] The common feature favouring fibre lengthening among all these systems involving main group metal additives seems to be the formation of a eutectic between SiO_2 and a few percent of the metal oxide We postulate that the formation of this liquid SiO_2–metal oxide phase acts as a flux to aid material flow into the fibre tail and allows fibres to continue growing at a lower temperature

This simple eutetic idea fails when applied to the transition metal chloride additives Transition metal oxides like TiO_2 form a eutectic with SiO_2 very similar to that formed with Al_2O_3, but mixing of vapours of transition metal chlorides or oxo-chlorides such as $TiCl_4$, $VOCl_3$, CrO_2Cl_2 or WCl_6 with the SiO before condensation gives solid products which contain mainly Monox-like fibres In most cases, the fibres are covered with nodules of solids rich in transition metal oxides With WCl_6 the nodules are only 1–5 nm in diameter [Figure 7(d)] Analysis by XPS shows oxidation states of 4+ for Ti, 5+ for V, 3+ for Cr and a mixture of 4+ and 6+ for W From chemical analysis there is as much free silicon in the fibres as with normal Monox but it is non-crystalline

So why the difference between main group and transition metal additives? The most important factor is likely to be the much lower solubility of transition metals than main-group metals in molten silicon This means that while main-group chlorides are reduced to metals on the hot silicon-rich growing tip and pass through in solution to scavenge oxygen from SiO_2 immediately behind the tip, reduction of transition metal chlorides is blocked because the metal silicide formed does not dissolve in or pass through the molten silicon Instead the transition metal chloride vapours seem only to attack the hot Monox fibres after they have formed, undergoing metathesis with silica on the surface to give the observed nodules of metal oxides

We think that the range of fibre morphologies that can be obtained from SiO condensation may be greater than for any other known substance We are still exploring practical uses of the various types of fibres that we can produce, particularly their potential as reinforcing fillers for plastics or rubbers Many of them can be dispersed by vigorous mechanical means in solutions of polymers with very little damage to the microfibres, *i e* they are quite strong, but bonding between polymers and the fibre surface needs to be improved to optimise their reinforcing properties

In all our preparations of SiO fibres so far we have used atmospheric pressure because it was most convenient but we now plan to investigate the condensation behaviour of SiO at pressures above and below atmospheric These studies should throw more light on the mechanism of fibre formation

5 New Low-temperature Solution Reactions of Silylenes

Silylenes, along with other carbene-like molecules, were among the first gaseous species formed under vacuum at high temperatures to be studied by the method of low-temperature condensation in the 1960s They were used to synthesise a large range of new organosilicon compounds and many major features of their chemistry under these conditions had been explored by the late 1970s [30] However, recently we chanced on a new facet of the chemistry of silylenes in the following way

Our aim was to make silicon oxoiodides, a previously unknown class of compound, to find if their thermal decomposition was a useful way of depositing high-quality silica layers for the electronics industry We considered condensing iodine vapour with SiO under vacuum at low temperatures but, to avoid the nuisance of evaporating the iodine, we chose to condense SiO into a solution of iodine in a solvent with a vapour pressure of 10 ^{1} Pa at its freezing point Tests showed that iodoethane or toluene were suitable solvents We hoped to avoid using carcinogenic iodoethane, so we tried toluene cooled to −90 °C From earlier work,[31] we knew that toluene reacted inefficiently with SiO at low temperatures partly by addition across the aromatic multiple bonds and partly by insertion into ring or methyl C–H bonds giving intractable solids but we felt it was likely that the reaction with I_2 would predominate

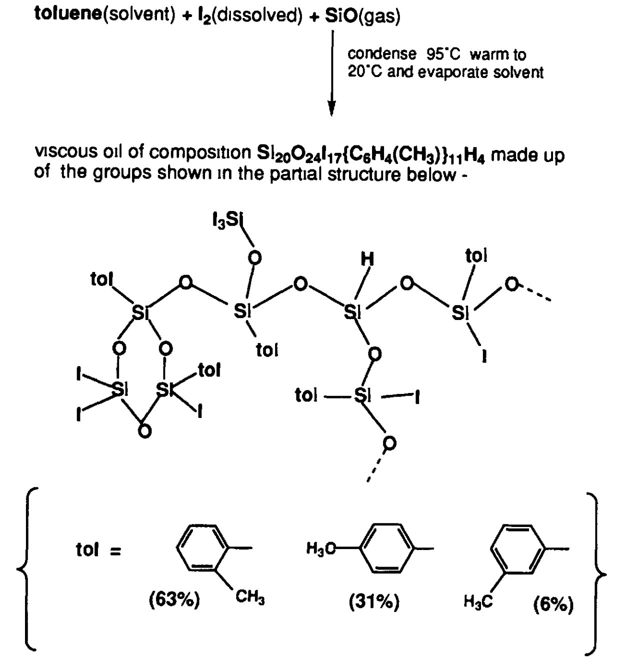


Figure 8 The formation of a polysiloxane from reaction of SiO gas with a solution of iodine in toluene at −95 °C

The result was quite different from our expectation The only reaction product was an oil of molecular mass around 3000 [32] A combination of MS, IR, ^{1}H, ^{13}C and ^{29}Si NMR, and chemical analysis studies on the product indicated that it was a polysiloxane with $C_6H_4(CH_3)$, I and H substituents on silicon in an overall composition close to $Si_{20}O_{24}I_{17}\{C_6H_4(CH_3)\}_{11}H_4$ The structure was complex apparently involving both ring and chain forms of the siloxane skeleton containing linked $XYSi(O-)_2$ units [$X=I$, $Y=C_6H_4(CH_3)$, H or I] with a few chain-terminating I_3SiO- groups and chain or ring branching $HSi(O-)_3$ or $ISi(O-)_3$ units (Figure 8) Carbon–silicon bonds had been formed exclusively with aromatic ring carbons, the predominant mono-substitution of H by Si on toluene gave relative proportions of the resulting *ortho*, *para* and *meta* isomers of 6 3 1

Subsequently, we found that the dihalogenosilylenes behave similarly [33] Condensation of SiF_2, $SiCl_2$ or $SiBr_2$ into solutions

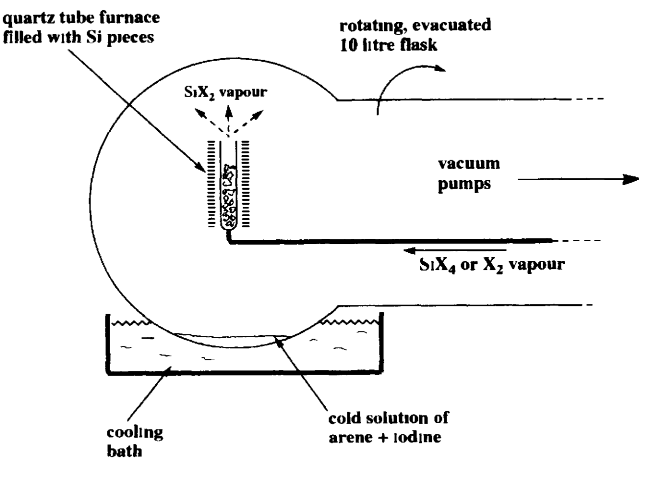


Figure 9 Apparatus used for reacting dihalosilylenes under vacuum with cold solutions

of iodine in toluene at –90 °C using the apparatus of Figure 9 results in efficient aromatic substitution reactions giving $C_6H_4(CH_3)SiX_2I$(X=F, Cl, Br) with respective *o p m* isomer ratios of 3 1 1, 10 4 3 and 5 2 2 When the toluene solution of I_2 is replaced by ICl in toluene in these reactions, the same reaction products are formed, *i e* there is no incorporation of chlorine from the ICl in the products

How do these reactions occur? The following is our current interpretation It has been known for many years that when I_2 is dissolved in benzene, toluene or other alkylbenzenes, complexation occurs and the polarised I_2 molecules are sandwiched between the planes of aromatic rings as shown in Figure 10 When an SiO or SiX_2 molecule condenses in the solution at −90 °C, addition of I_2 to give $SiOI_2$ or SiX_2I_2 definitely does not occur to any appreciable extent Instead, the SiO or SiX_2 may act as a nucleophile, approaching the positively charged end of the polarised I_2 molecule and forming toluene $SiOI^+$ I^- toluene or toluene SiX_2I^+ I^- toluene moieties within the sandwich structure, which rearrange as shown in Fig 10 so the positive charge is on the toluene This effectively electrophilic attack liberates H^+ which associates with the I^- There is at present considerable interest in silyl cations and an indication from the work of Schleyer[34] that the interaction between an arene and a silyl cation could yield an intermediate of the type shown in Figure 10

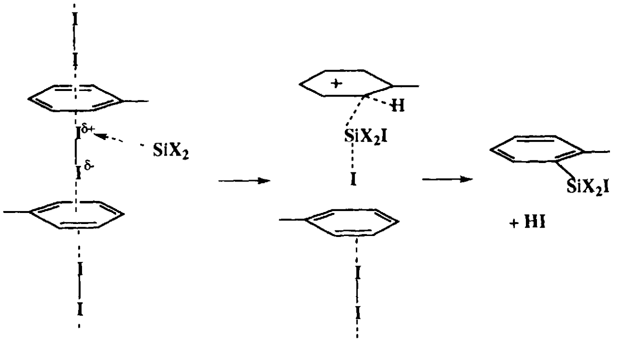


Figure 10 A proposal for the mechanism of the reaction of silylenes with toluene and iodine

In toluene solution, ICl is complexed in the same way as I_2 The fact that ICl reacts the same as I_2 provides strong evidence against a possible alternative mechanistic explanation involving free radicals For if the reaction of ICl and SiX_2 yielded free radicals, $SiX_2Cl^\bullet + I^\bullet$ would be more thermodynamically favoured than $SiX_2I^\bullet + Cl^\bullet$ The absence of chlorine incorporation in the products shows that $SiX_2Cl^\bullet$ cannot be the attacking species

Overall, these iodine-induced reactions of silylenes with toluene or with other alkylbenzenes provide (a) the most direct way known of forming a silicone oil – albeit a very reactive one as it contains Si–I in addition to Si–aryl bonds but the Si–I can be quantitatively converted to Si–OR by reaction with an ether at low temperatures, and (b) a way of making chemically reactive arylSiX_2I products, which are generally new compounds since they are hard to prepare conventionally

What of the silicon oxoiodides? Did we prepare a liquid polymer of nominal composition $(SiOI_2)_n$ by condensing SiO into a solution of iodine in iodoethane at −100 °C which was shown by ^{29}Si NMR to contain mainly $I_2Si(O–)_2$ units with some branching $ISi(O–)_3$ units and terminal I_3SiO–units On strong heating under vacuum it vaporised yielding mainly cyclic $Si_3O_3I_6$ but this has proved very reluctant to decompose cleanly on hot surfaces to SiO_2 and SiI_4 So the original objectives of our study proved to be worthless, but a rich new vein of silylene chemistry has been discovered in the process

Acknowledgements I am very grateful to all my co-workers, post-doctoral, post-graduate and undergraduate named in the references, who have carried out the work described and to SERC and Elkem Chemicals who supported some of these coworkers and the research

6 References

1 P S Skell, L D Westcott, J P Golstein and R R Engel, *J Am Chem Soc* , 1965, **87**, 2829
2 P L Timms, *Chem Commun* , 1969, 1033
3 J R Blackborow and D Young, *Metal Vapour Synthesis in Organometallic Chemistry*, Springer Verlag, Berlin 1979
4 P L Timms, in *High Energy Processes in Organometallic Chemistry*, ed K S Suslick, ACS Symposium Series 333, 1987, p 1
5 K J Klabunde, *Free Atoms, Clusters and Nanoscale Particles*, Academic Press, London, 1994 K J Klabunde, *Chemistry of Free Atoms and Particles*, Academic Press, 1980
6 H W Kroto, *Angew Chem , Int Ed Engl* , 1992, **31**, 111
7 R M Pope, S L VanOrden, B T Cooper and S W Buckner, *Organometallics*, 1992, **11**, 2001
8 M D Morse, M E Gensic, J R Heath and R E Smalley, *J Chem Phys* , 1985, **83**, 2293
9 S Iijima, *Nature*, 1991, **354**, 56, N S Chopra, R J Luyken, K Cherry, V H Crespi, M L Cohen, S G Louie and A Zettl, *Science*, 1995, **269**, 966
10 U E Wiersum, *Recl Trav Chim Pays Bas*, 1982, **101**, 317, 365
11 M J Almond and A J Downs, *Spectroscopy of Matrix Isolated Species*, ed R J H Clark and R E Hester (*Advances in Spectroscopy Vol 17*), Wiley, Chichester, 1989
12 C G Francis and P L Timms, *J Chem Soc , Dalton Trans* , 1980, 1980
13 M L H Green, *J Organomet Chem* , 1980, **200**, 119
14 M L H Green, D O'Hare, P Mountfield and J G Watkins, *J Chem Soc , Dalton Trans* , 1991, 1705
15 U Zenneck, *Angew Chem , Int Ed Engl* , 1990, **29**, 126
16 Z Yao, K J Klabunde and A S Asirvatham, *Inorg Chem* 1995, **34**, 5289
17 J G Brennan, F G N Cloke, A A Sameh and A Kaikin, *J Chem Soc , Chem Commun* , 1987, 1668
18 F G N Cloke, M F Lappert, G A Lawless and A C Swain, *J Chem Soc , Chem Commun* , 1987, 1167
19 R Middleton, J R Hull, S R Simpson, C H Tomlinson and P L Timms, *J Chem Soc , Dalton Trans* , 1973, 120, T S Tan and M J McGlinchey, *J Chem Soc , Chem Commun* , 1976, 155
20 J J Barker, A G Orpen, A J Seeley, and P L Timms, *J Chem Soc Dalton Trans* , 1993, 3097
21 A Martin, A G Orpen, A J Seeley and P L Timms, *J Chem Soc Dalton Trans* , 1994, 2251
22 A J Seeley, S Hudson, P D Sykes, W B Weise and P L Timms, *J Organomet Chem* , 1995, **487**, 167
23 M Andrews, S Matlar and G A Ozin, *J Chem Phys* , 1991, **95**, 2738
24 T W Bell, M Helliwell, M G Partridge and R N Perutz, *Organometallics*, 1992, **11**, 1911
25 H N Potter, *Trans Am Electrochem Soc* , 1907, **12**, 191
26 D S Sears, *US Pat* 2 865 881 and 2 865 882, 1958
27 S R Church, K Chown, T Lippard, D Mulligan, S Sakanishi, P L Timms and G C Allen, *J Mater Chem* , 1995, **5**, 757
28 A Songsasen and P L Timms, unpublished results, 1995
29 J A Nuth and B Donn, *J Chem Phys* , 1982, **77**, 2639
30 C Lui and T Hwang, *Adv Inorg Chem Radiochem* , 1985, **29**, 1
31 E T Schaschel, D N Gray and P L Timms, *J Organomet Chem* , 1972, **35**, 69, W N Rowlands, Ph D Thesis, University of Bristol, 1989
32 W N Rowlands and P L Timms, *J Chem Soc , Chem Commun* , 1989, 1432, P L Timms and W N Rowlands, *U S Pat* 5,034,554 (1991)
33 S R Church, C G Davies, R Lumen, P A Mounier, G Saint and P L Timms, *J Chem Soc , Dalton Trans* , 1996, 257
34 P v-R Schleyer, P Buzek, T Muller, Y Apeloig and H-U Siehl, *Angew Chem Int Ed Engl* , 1993, **32**, 1471