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Thermal stability and the formation of conducting materials from tricobalt–carbyne clusters

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The conductivity of microcrystalline mono- or bis-carbyne capped tricobalt clusters and a preliminary study of the physical properties of the thermally decomposed materials are presented. Solid materials with high conductivities are produced by the controlled decomposition of the non-conducting carbonyl clusters in which there are two cluster units or an alkyne/cluster system. Processes leading to conducting solids were studied by thermogravimetric, mass spectral, DRIFT and SEM techniques. Bi-capped clusters are thermally stable insulators but it is suggested that doped materials will show increased conductivity.

Keywords: Clusters, thermal decomposition, conductivity

INTRODUCTION

Strategies for the assembly of structure-enforced and/or doped-structure electrically conductive arrays have been proposed for a wide variety of inorganic and organic systems.[1,2] Organometallic compounds usually lack the classical features of conducting materials such as partially filled, spatially delocalized electronic energy levels[3] although structure-enforced aggregated materials (e.g. 'stacked' systems) can allow electrical charge to be transported in the solid state.[3,4] Volatile organometallic compounds, on the other hand, have exciting possibilities as sources of conducting films or solids via decomposition techniques[5–8] as they can circumvent the need for high decomposition temperatures. Whilst the thermal decomposition of supported metal carbonyl clusters does yield highly dispersed metal catalysts, which have been extensively studied by a range of physical techniques,[9] it is only recently that the increased metal content of clusters has been utilized to prepare metal films.[8] Capped metal carbonyl clusters offer the possibility of incorpoating non-metal atoms into the thermally decomposed materials in a controlled way; alternatively, the clusters can be organized into a conductive array using standard synthetic techniques. These are the thrusts of our present research programme.

Electrochemical studies on compounds in which there are two reducible or oxidizable cluster units in the molecular framework, connected by carbyne or alkyne groups, have clearly demonstrated that there is interaction in the electrochemical sense between the cluster units.[10–13] This interaction is not a function of the electron 'richness' of the valence levels as it is observed with capped carbonyl clusters containing the $CCo_3(CO)_9$ unit and bi-capped cyclopentadienyl clusters $CCo_3(Cp)_3C$. Clearly, the interaction is a manifestation of the delocalized character of the upper valence levels which incorporate metal, carbyne and ligand contributions.[14,15] The carbyne functionality provides the electronic link between the valence levels. Thus within the individual molecules there would appear to be few 'hills' and 'valleys' to hinder extended electronic charge movement. To obtain a bulk conductive array these molecules need to be arranged in close proximity (e.g. stacked) or linked as polymers so that a progression of valence bands can be built up to a bandwidth. A second prerequisite for conductively arrayed molecules is the need for some molecules to have fractionally occupied valence shells. The facile reduction (carbonyl)[16] and oxidation (cyclopentadienyl)[11,12] of capped tricobalt clusters allows for mixed valency in the solid phase and may be achieved by chemical or electrochemical methods. This mixed valence has been demonstrated for both $CCo_3(CO)_9$[17,18] and $CCo_3(Cp)_3C$[11] systems in single molecules.

In this paper we look at the fundamental conduction properties of mono- and bi-capped tricobalt clusters as microcrystalline solids and present a preliminary investigation of the feasibility of these metal clusters facilitating electronic charge movement in conducting materials.

RESULTS

Clusters available from recent synthetic studies were used in this work;[11–13,19,20] their molecular structures (**1**–**6**) are shown in Fig. 1.

Large single crystals of these clusters suitable for direct conductivity measurements could not be prepared. Initial spot frequency measurements at 100 Hz of pressed discs of microcrystalline material indicated that all clusters had conductivities in the order of 10^{-13} S cm^{-1} irrespective of the structure or extent of delocalization between alkyne-linked cluster units. These small conductivities presented problems in the evaluation of the DC data since the conductivity may merely produce a value corresponding to the most resistive component of a particular sample, which may be a function of geometry rather than a property of the solid itself.

Impedance spectroscopy which uses alternating currents over a range of frequencies[21] was therefore the preferred technique as, in principle, it can allow an assessment of the overall resistivity. Hodge's method[22] was used to analyse the data. The complex impedance (Z'') and modulus (M'') spectra detail complementary information by placing different emphasis on bulk and interfacial effects. Moreover, a comparison of data from loosely and densely packed samples can identify peaks relating to intergranular effects as these tend to shift to lower frequencies as the interparticle resistance decreases.

Conductivity and thermal stability of biscarbyne complexes

Biscarbyne complexes **1**–**3** proved to be thermally and oxidatively stable, **1** melting at 200°C whereas **2** and **3** did not melt up to the maximum temperature of the experiment (250°C). Initial scans indicated that these solids were behaving as a single resistive component, but changes in impedance profiles took place on cooling then reheating the samples above 192°C (**1**) or 150°C (**2**, **3**).

Plots of the complex impedance and complex modulus are non-reproducible, moving to lower frequencies (Fig. 2) as the sample geometry changes (softening). This suggests that the observed peaks are associated with intergranular effects. The asymmetries of the complex impedance and modulus spectra were compatible with at least *two* processes. Plots of $F(Z_{max})$ against $1/T$ at temperatures for which the sample geometry remains unchanged displayed two lines of equal slope; for **2** the activation energy for the two processes was 339 kJ mol^{-1} (Fig. 3). Diffuse reflectance FT-IR (DRIFTS), X-ray, elemental and NMR analyses of the heated samples gave no evidence for a chemical change and there is no doubt that the two processes are a result of intergranular effects.

Cluster **3** has two potential oxidizable sites, the ferrocene moiety as well as the Co_3Cp_3 core.[11] Electrochemical data show that the cluster core is the most readily oxidized centre but charge-transfer to species such as TCNQ is stereochemically difficult whereas ferrocene–TCNQ adducts are well-characterized.[23] Accordingly, a **3**–TCNQ compound was synthesized in an attempt to induce holes in the valence/conduction bands. Spectral data were consistent with the formation of a 3^+–$TCNQ^-$ complex but no conducting materials were found up to the point at which thermal decomposition took place (~100°C), irrespective of the mole ratio.

When silver paint was used to improve the contact between **1**–**3** and electrodes for impedance spectroscopy there was an increase in conductivity by several orders of magnitude. We suggest that arises from Ag^+ impurities in the paint which can act both as a Lewis acid and oxidizing agent.

$$RCCo_3Cp_3CR' + Ag^+$$

$$\rightarrow \text{edge-bridged } [Ag\text{-}RCCo_3Cp_3CR']^+$$

$$RCCo_3Cp_3CR' + Ag^+ \rightarrow [RCCo_3Cp_3CR']^+ + Ag$$

Edge-bridging by H^+ and Ag^+ ions has been noted previously[11,13] with these clusters. These reactions may produce islands of metallic silver at the surface of the cluster particles, reducing the intergranular resistivity, but the mechanism of the dispersion of Ag/Ag^+ throughout the cluster material is unknown. Nonetheless, this observation does point to a method for producing thermally stable, doped, conducting solids.

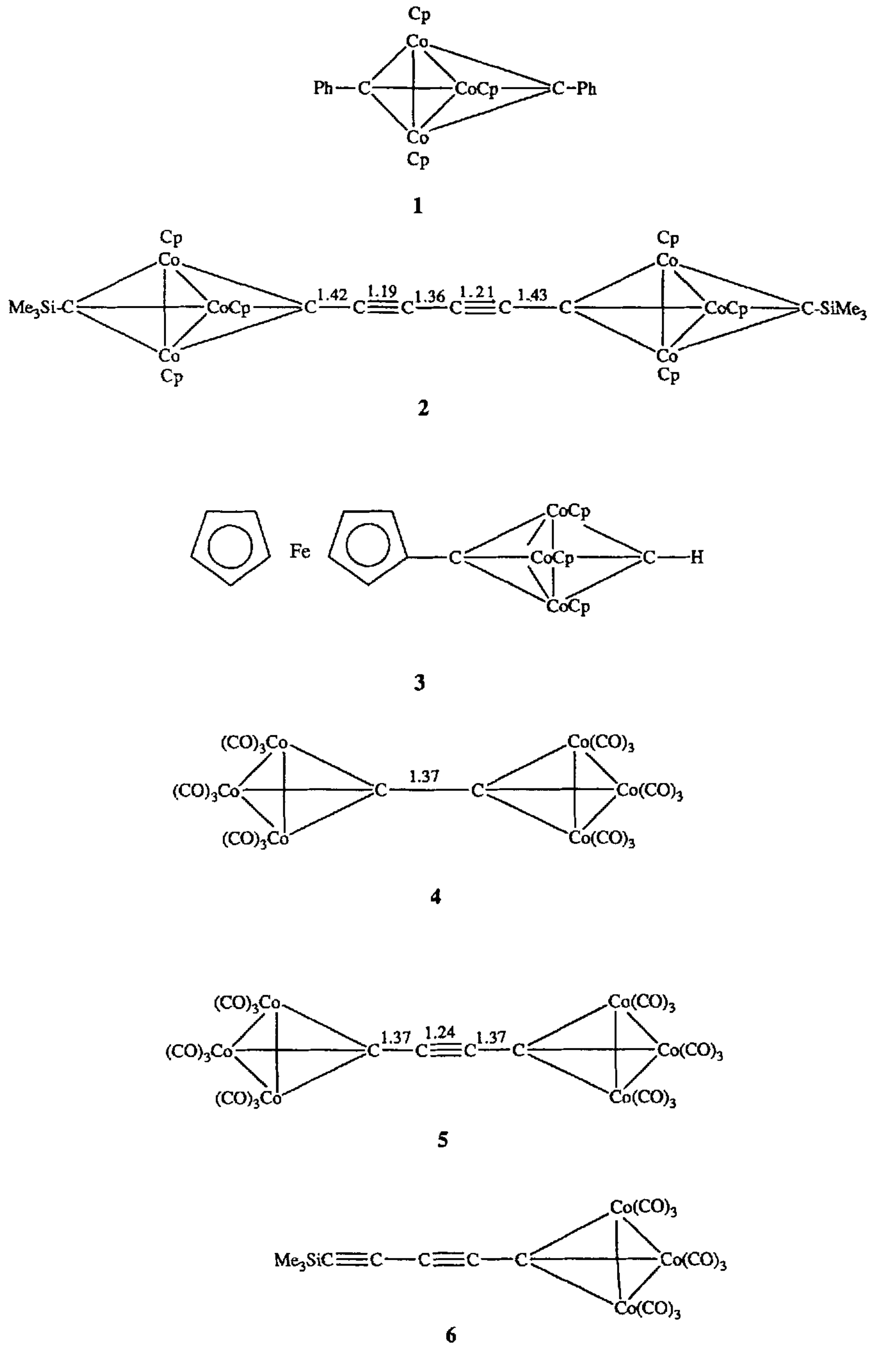

Figure 1

Alkylidynetricobalt carbonyl clusters

Prototypal $YCCo_3(CO)_9$ clusters (Y = arene, alkyl, H, Cl) show a range of thermal and oxidative stability but in general are thermally stable under argon, CO or *in vacuo* to temperatures >130°C. During the course of impedance measurements on alkylidynetricobalt carbonyl clusters **4–6**

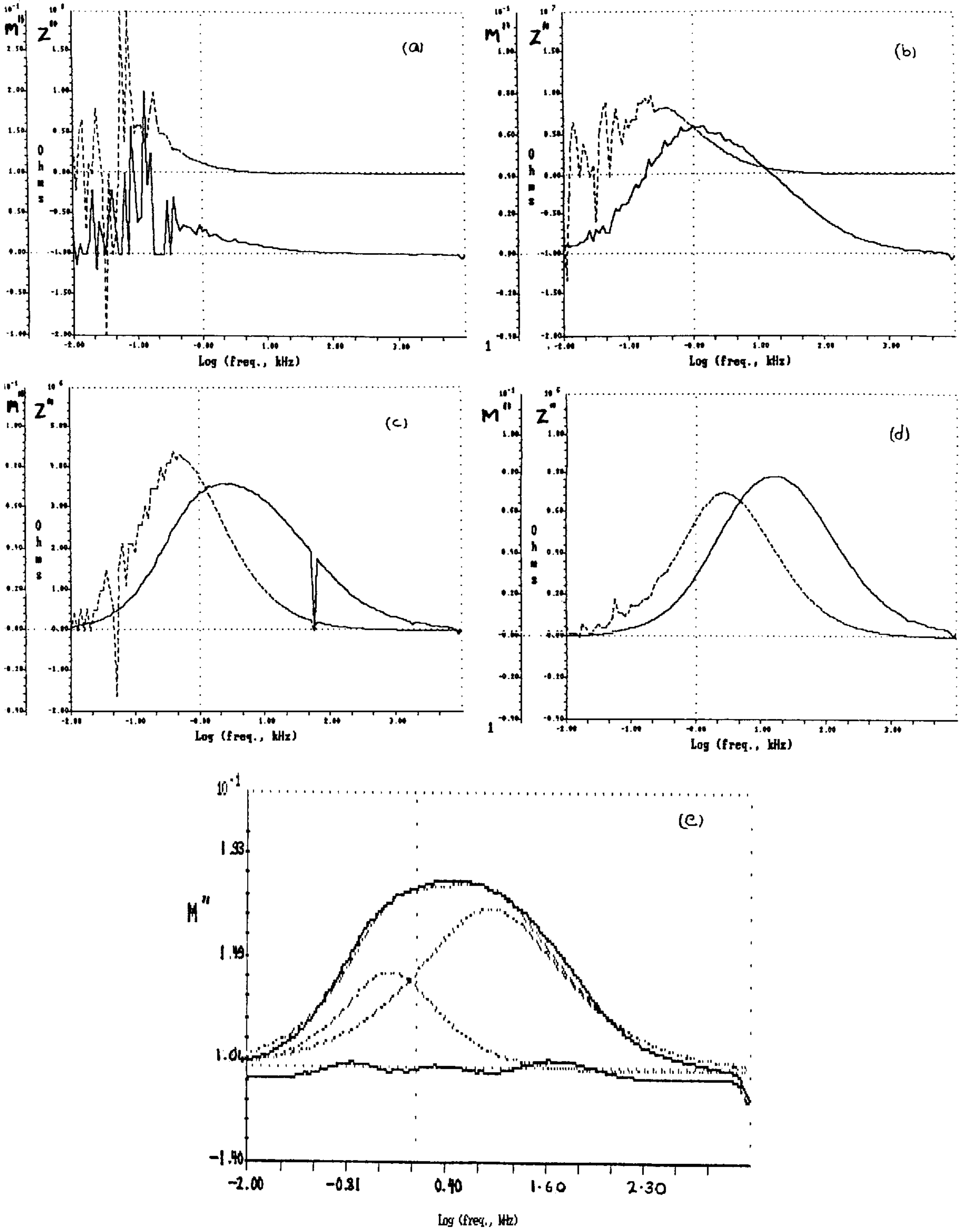

Figure 2 Representative M'' and Z'' impedance spectra for **2**. (a) 66°C; (b) 134°C; (c) 152°C; (d) 222°C; (e) simulation of complex modulus for **1** showing the possible resolution into two peaks.

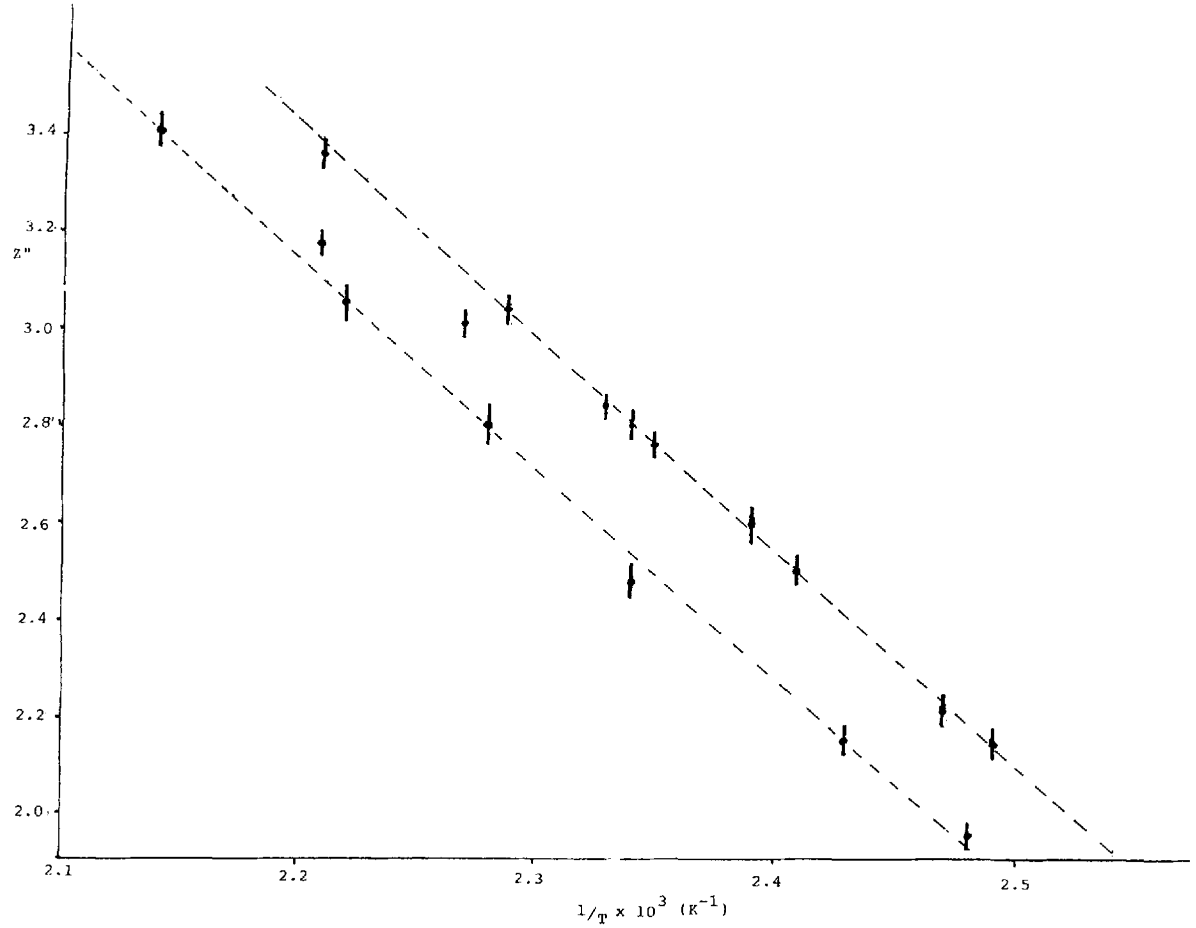

Figure 3 Plot of log ω_{max} for Z'' vs $1/T$ ($\times 10^{-3}$, K^{-1}) for cluster **1**.

which incorporated two Co_3 units per molecule, or an acetylene functionality, it became clear that the thermal decomposition of these clusters occurred at relatively low temperatures (~90°C).

The most significant observation was that the conductivity of the clusters dramatically increased at the decomposition temperature: thus, the conductivity of **4**–**6** increased by a factor of 10^9 at 100°C giving the samples 'metallic' conductivity. Furthermore, the DRIFT spectra of the 'decomposed' materials still showed ν(CO) bands typical of cluster structures and were largely soluble in non-aqueous solvents, indicating for the first time that thermal decomposition of the alkylidyne clusters could yield structure-enforced conducting materials. It should be emphasized that reproducibility of conduction properties was possible providing the conditions were strictly controlled.

To identify the physical basis for the increased conductivity, the system was investigated by mass and infrared spectral, thermogravimetric, XRD and SEM analytical techniques. Thermogravimetric and mass spectral analysis of the changes that occurred on thermal decomposition of **4**–**6** closely simulated the conditions of the impedance experiments. For thermogravimetric analysis the sample temperature was increased at 5°C min^{-1} until 140°C and then maintained at 140 °C for 6 h in an argon flow. Rapid weight loss occurs at ~80°C (this does not vary with cluster structure) with the maximum rate of weight loss around 90°C. For **5** 68 % of initial weight was reached after 5 h at 140°C, which does not equate with the complete loss of coordinated CO. Nevertheless, X-ray powder diffraction of the samples showed them to be amorphous and

DRIFT spectra gave only weak ν(CO) bands. Similarly, amorphous solids with little evidence for coordinated CO were obtained from **4** and **6**. When samples of **5** were heated directly for 6 h to 140°C under argon or *in vacuo* the amorphous products still contained ~13 % of carbon and occasionally ~1 % of hydrogen (presumably from traces of water). SEM micrographs of the granular surface suggest that there was an even dispersion of particles while preliminary AES did not support the formation of a carbide phase. Most significantly, the conductivities of these amorphous solids were only slightly higher than those of the pure clusters (cf. samples from controlled decomposition as described below).

Decomposition of non-capped clusters [e.g. $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$] supported on oxide catalysts is believed to proceed via a primary pathway at low temperatures (<130 °C), characterized by the elimination of CO and partial oxidation of metal on the surface, and a secondary high-temperature pathway.[9] During the latter pathway, surface carbon can hinder the aggregation to form larger metallic crystallites. Thermogravimetric results on **4** and **6** can be more closely aligned with these secondary processes for supported clusters and the relatively high carbon content compared with supported systems may be due to the lack of oxygen sources (e.g. OH). The highly dispersed surface carbon may well protect the small, active metallic particles from oxidation (both physically and by providing a reducing environment), which in turn could result in catalytic material of high activity. Further investigation of these materials is contemplated.

In separate experiments **4**–**6** were heated in an argon flow at controlled rates to a maximum temperature of 140°C, held at this temperature for only 1 h (compared with 6 h for the thermogravimetric analysis), and the volatiles monitored by mass spectral analysis. Decomposition in this manner, which uses exactly the procedure used for the impedance measurements, invariably gave materials with X-ray powder diffraction patterns. The materials produced in the temperature range above 90°C had conductivities matching those obtained during the impedance runs. Figure 4 shows the variation in volatiles with time for a representative cluster **5**.

No metal fragments could be identified in the mass spectra (i.e. above 60 mass units), which is not unexpected, given the low thermal decomposition temperature. The principal components were CO, CO_2, O_2, and H_2O; the absence of hydrocarbons, which are often produced in an environment of metal particles and an OH source,[9] is noteworthy. Loss of CO was initially detected at 75°C and continued at an increased

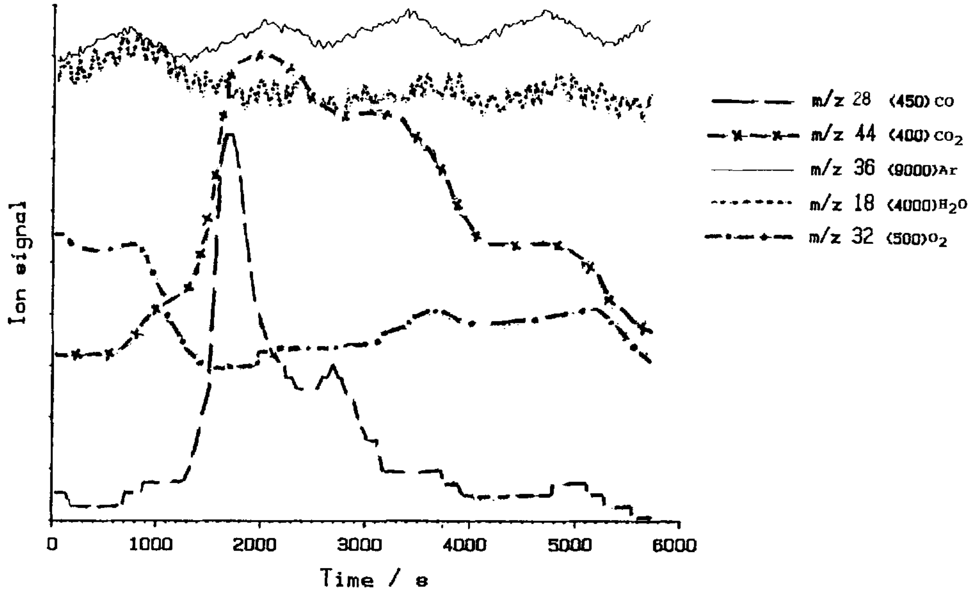

Figure 4 Mass spectral analysis of volatiles emitted during the thermal decomposition of **5** under argon. The time scale represents a temperature increase from 20°C to 140°C with the sample held at 140°C for 1 h.

rate until 140°C. Thus the CO emission precedes the onset of metallic conductivity by approximately 15°C and occurs at a much lower temperature than the CO emission from prototypal $YCCo^3(CO)_9$ clusters; however, CO emission occurs at a similar temperature for **4** and **6**. At a constant temperature of 140°C there was a rapid decrease in CO emission to a zero level after 1 h. The amount of CO_2 produced closely tracked that of CO emission at the early stage of decomposition but CO_2 emission increased in the latter stages. An initial decrease in O_2 content presumably reflects a catalysed conversion of CO to CO_2, but the amount rose later in the experiment suggesting that the increased CO_2 evolution came from another reaction. Similar observations were found for **4** and **6**.

Thus, at low temperature, oxygen reacts with surface cobalt giving the Co–O species which in turn can react with the liberated CO:

$$2\mathrm{Co{-}CO} \rightarrow 2\mathrm{Co} + \mathrm{O_2} \rightarrow 2\mathrm{Co{-}O_{(surf)}}$$

$$\mathrm{CO{-}O_{(surf)}} + \mathrm{CO} = \mathrm{CO_2} + \mathrm{Co}$$

$$\mathrm{CO} + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{H_2}$$

At higher temperatures the CO shift reaction could dominate. These reactions contribute to the removal of surface metal oxide, although the absence of an accessible structural OH group, as found with supported clusters, may prevent surface carbon or carbide being readily removed.

Throughout the mass spectral experiment, and indeed whenever highly conducting materials are formed, DRIFT spectra showed clearly that only partial decarbonylation had occurred. The first significant change in the ν(CO) profile occurs round the onset of conductivity at 90°C (Fig. 5) with the appearance of bands at lower energy than those of the parent.[13] Broad bands which grow in intensity with time in the region 1600–1300 $\mathrm{cm^{-1}}$ are similar to those seen in the DRIFT spectra of the amorphous solids and, while they may be associated with the formation of metal oxide or carbonaceous material, we have not been able to eliminate the possibility that they are an artefact of the DRIFT procedure—certainly, the intensity of these bands is non-reproducible and in some cases they are absent in 140°C samples. The intensities of the ν(CO) bands progressively decrease with increase in temperature but, once conductivity is observed, *the profile does not change* even at the point of zero CO emission. Furthermore, the same 'terminal' DRIFT spectrum was observed irrespective of the type of sample preparation and the ν(CO) bands at lower energy typically indicate a Co_3C structure of lower symmetry and/or lower cobalt coordination number.[25] Clusters identified by successive solvent extraction were **4** and **5** in small amounts (i.e. it appearts that desilylation occurred with **6**) and trace amounts of unidentified cluster compounds. Clearly, thermal decomposition at temperatures <140°C does not cause appreciable fragmentation of the Co_3C unit (the typical decomposition route in solution or for prototypal $YCCo_3(CO)_9$ compounds) but some reversible rearrangement of the C_nCo_3 moiety may take place. Nonetheless, *conductivity is associated with partial decarbonylation* of the clusters and intermolecular association where the delocalized nature of the clusters allow electronic charge transfer between particles.

Scanning electron micrographs of amorphous non-conducting materials showed a uniform granular surface composed of particles 1000–5000 μm in size, whereas those of conducting materials, whilst granular and of similar size to the amorphous material, contained 'islands' of denser materials (Fig. 6). Electron microprobe analysis of the 'islands' indicated that they are cobalt-rich and we were able to confirm the presence of cobalt metal but not cobalt oxide phases.

CONCLUSION

The carbyne-capped clusters **1–6** offer two distinct scenarios for the production of conducting materials. Bi-capped $C_2Co_3Cp_3$ entities will need to be incorporated in doped materials but they will be thermally and oxidatively stable. Genesis of reactive and conducting materials or films incorporating the mono-capped Co_3C is possible via the controlled thermal decomposition of carbyne-linked clusters. The surprising feature of the latter materials is the reproducibility of the conductivity and spectral data, given that the conductivity apparently arises from a reduction in the intergranular resistance by 'islands' of metallic particles, although reduction by active cobalt metal to produce cluster-centred holes to assist electron transfer cannot be eliminated. Further work will explore this concept.

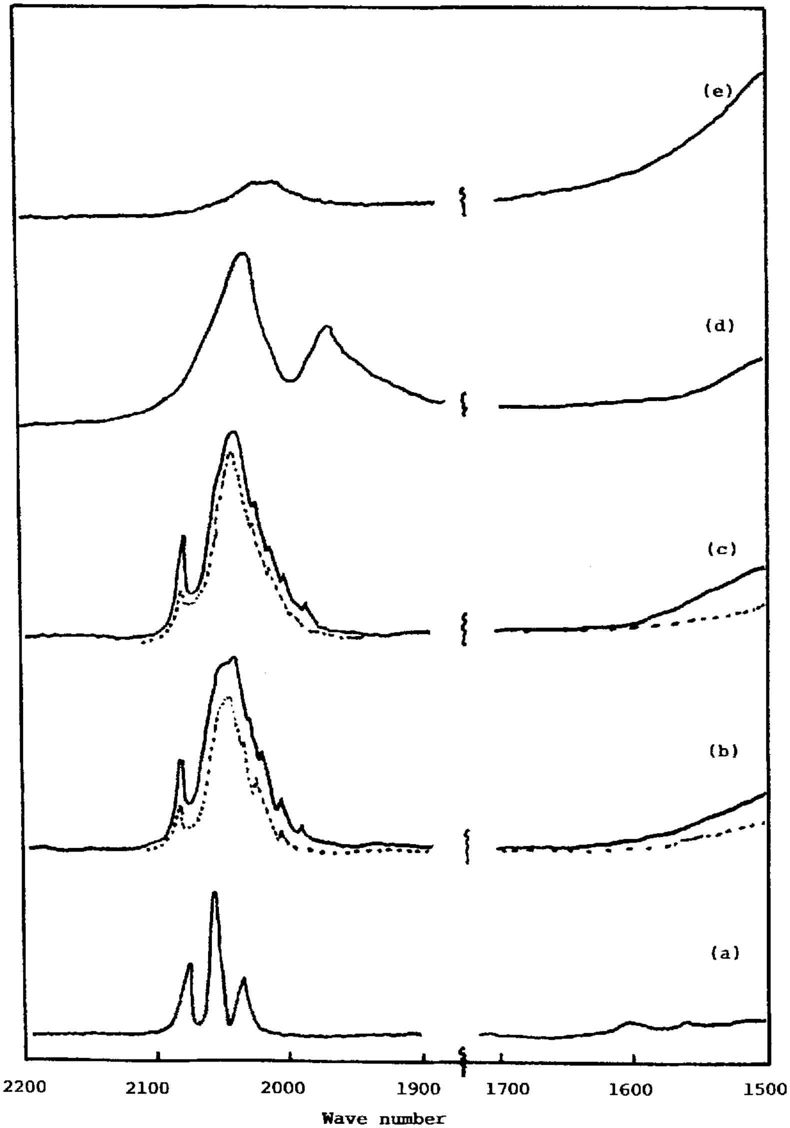

Figure 5 DRIFT spectra between 2200 and 1500 cm^{-1} in KBr matrix. (a) 5; (b) terminal material from 5 impedance runs; (c) terminal material from 5 mass spectral runs; (d) terminal material from 4 impedance runs; (e) amorphous terminal material from 5 thermogravimetric runs. Dotted-line spectra refers to samples at onset of conductivity.

EXPERIMENTAL

The compounds $Ph_2C_2Co_3Cp_2$ (**1**),[20] $[Me_3SiC_2Co_3Cp_3C_2]_2$ (**2**),[12] $Fe(H)C_2Co_3Cp_3$ (**3**),[11] $[CCo_3(CO)_9]_2$ (**4**),[13] $C_2[CCo_3(CO)_9]_2$ (**5**)[13] and $Me_3SiC_4CCo_3(CO)_9$ (**6**)[13] were prepared according to literature procedures. Special care was taken to obain samples of maximum purity as shown by TLC, FAB MS and solution IR spectra. Repeated recrystallization from hexane was the best procedure but it was essential to extract the microcrystalline material from solution as quickly as possible under anaerobic conditions in order to obtain reproducible impedance data for the materials of low conductivity.

The adduct $[Fe(H)C_2Co_3Cp_3]^+TCNQ^-$ was prepared by the direct equimolar reaction between the donor and acceptor in acetonitrile. Removal of the solvent gave a green microcrystalline material. Found: C, 58.90; H, 4.12. Calcd for

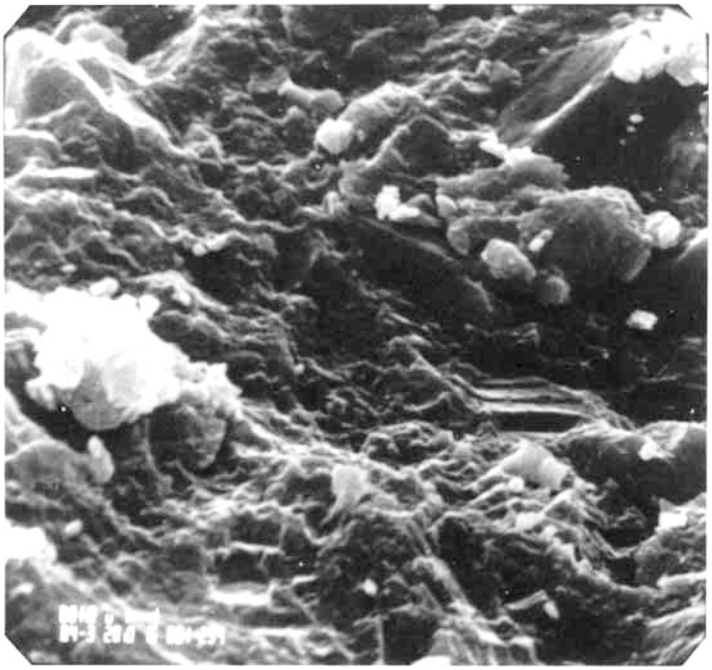

Figure 6 SEM of highly conducting material produced by controlled thermal decomposition of 5 at 100°C.

$C_{39}H_{30}Co_3FeN_4$: C, 59.46; H, 3.81%. The presence of $TCNQ^-$ was confirmed by IR (typical ν(CN) band at 2192 cm^{-1}), electronic (bands at ~720 and 830 nm) and ESR spectra.[26]

Physical measurements

X-ray diffraction

Material from controlled thermal decomposition or impedance experiments was finely ground and pressed on to a glass slide which was then mounted in a Philips X-ray powder diffractometer. Either a Fe or Co source was used and data were collected over a $4° < 2\theta < 70°$ range.

Diffuse reflectance infrared spectra

Samples were prepared by grinding a small amount of sample (~3 mg) with KBr (~0.3 g) and the spectra run using a Barnes DRIFT attachment on a Digilab FX-60 FTIR spectrometer. The heated samples were successively extracted with CH_2Cl_2, $CHCl_3$, acetone, methanol and water and the solution IR spectra recorded to identify cluster complexes.

Mass spectral measurements

A weighed sample of cluster (~10 mg) was placed in a heating tube under a flow of argon (15 ml s^{-1}). The tube was heated in a furnace controlled to raise the temperature to 140°C at 5°C min^{-1}. The argon flow was piped to a Hewlett–Packard HP 35 Spectra EL extranuclear mass spectrometer which recorded data between 0 and 150 amu at 1–2-minute intervals. A background count prior to the tube being heated was used as reference.

Thermogravimetric analysis

The cluster (~6 mg) was weighed in a Pt/Au cup of a Stanton Redcroft TG-770 thermobalance. An argon flow (15 ml s^{-1}) was maintained throughout the experiment. The temperature was increased to 140°C at a rate of 5°C min^{-1} and the weight of the sample monitored on a chart recorder.

SEM measurements

Samples of parent and thermally decomposed clusters were prepared by standard SEM techniques and miocrographs recorded on a JEOL 840 SEM. It was established that gold sputtering did not alter the sample (cf. silver paint for electrodes).

Impedance data

Samples were prepared by pressing 80 mg of finely ground cluster, using a pressure of 3.5 tonnes, in a 12.9 mm die. This produced discs of

~0.4 mm thickness which were then accurately measured using microcalipers. Spectral data on these pressed discs showed that no molecular change had occurred. The cell for impedance measurements comprised two flat polished electrodes held between glass mounts, held together by springs. The cell was placed inside a small furnace which was controlled using a copper–constantin thermocouple; the whole cell was flushed with argon during the experiment. The temperature of the sample was increased in 10°C stages allowing 10–15 min for the system to read equilibrium. A Hewlett–Packard impedance analyser was used to collect 121 conductance and capacitance readings between 10 Hz and 10 MHz at an oscillator level of 0.1 V. At random intervals the temperature was lowered by at least 20°C to test the reproducibility. Data were stored on disk and manipulated using IBM-compatible programs, IMP, ADMIT, SLPOTX (written by Dr J. Tallon, PEL, DSIR, Wellington, New Zealand) to produce plots of M'' and Z'' as a function of $\log f$ (kHZ) at a given temperature.

With the introduction of frequency-dependency elements the ASC response is usually analysed in the form of complex impedance plots. Hodges method[22] utilizes the complex impedance (Z'') and modulus (M'') spectra where for an ideal electrolyte the peak maxima coincide at an angular frequency

$$\omega_{\max} = (\tau_0)^{-1}$$

(τ is the conductivity relaxation time) and appear as symmetric Debye peaks. Normally the peaks are broad and the maxima do not coincide due to a distribution in relaxation times. The peak heights of Z'' and M'' are proportional to the resistance and (capacitance)$^{-1}$ respectively and thus the impedance and modulus spectra detail complementary information with different emphasis on bulk and interfacial effects. Comparison of data from loosely packed and densely-packed samples can identify peaks relating to intergranular effects as these tend to shift to lower frequencies as the interparticle resisance decreases. Data obtained over a range of temperatures give Arrhenius parameters and assist in evaluating changes in sample geometry. In this work the emphasis was on the resistance, and relative importance of intra- and inter-granular effects. Full data are available from the authors.

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