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Formation of a Superconducting Mixture of β-Mo_2C Nanoparticles and Carbon Nanotubes in an Amorphous Matrix of Molybdenum Compounds by the Pyrolysis of a Molybdenum Derivative of a Carboranylenesiloxane

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A pyrolytic treatment (to 1000 °C) of the organometallic reaction product of the thermo-oxidatively stable carboranylenesiloxane, **1**, and cyclopentadienylmolybdenum tricarbonyl dimer, $Cp_2Mo_2(CO)_6$, was discovered to yield nanoparticles of Mo_2C concomitantly with carbon nanotubes in an amorphous matrix of Mo compounds. X-ray diffraction studies revealed that the Mo_2C nanoparticles possess the hexagonal phase. A peak fit analysis using a Gaussian distribution function of the X-ray diffraction data revealed that 80% of the total molybdenum units in the mixture exist as β-Mo_2C nanoparticles. The presence of the carbon nanotubes dispersed in the amorphous matrix was determined by both X-ray diffraction and high-resolution TEM analyses. The pyrolytic residue was determined to be superconducting with a critical temperature (T_c) of 8 K. A comparative analysis of T_c value of the residue and the reported individual T_c values of the various components in the residue (β-Mo_2C, carbon nanotubes, and some possible Mo compounds) pointed to β-Mo_2C as the most probable cause for the superconductivity in the residue.

Introduction

Molybdenum carbide (Mo_2C), which was discovered along with several binary and ternary compounds by the seminal work of Meissner and co-workers on superconductors,[1] has recently attracted increased attention for its ceramic and catalytic applications.[2] Mo_2C has been shown to be a very active catalyst for methane reforming,[3] aromatization,[4] dehydrogenation,[5] and hydrodesulfurization (HDS).[6] Many procedures have been developed for the synthesis of high surface area molybdenum carbide such as gas-phase reactions of volatile metal compounds,[7a] reactions of gaseous reagents with solid-state metal compounds,[7b] and solution reactions,[7c] with the most widely used being the gas-phase carburization of molybdenum oxides.[7d] Mo_2C is also formed during a binary transition metal (Co−Mo or Fe−Mo)-catalyzed synthesis of carbon nanotubes by CVD from a carbon feedstock (e.g., hydrocarbon or CO) and heat.[8] It has been reported that even though the stoichiometry of bulk molybdenum carbide is Mo_2C, its phase diagram exhibits a wide range of Mo/C stoichiometry including MoC (1:1) phases with hexagonal (γ-MoC, η-MoC) and cubic (δ-MoC) structures.[9] Surfaces of the molybdenum carbide catalyst can be carbon or metal terminated, and nonstoichiometric Mo/C ratios are often observed on carburized Mo surfaces that exhibit catalytic reactivity that is strongly dependent on the surface composition and annealing temperature.[10] Nanoparticles of Mo_2C offer the possibility for creating a wider variation in surface structure and composition, which could result in further modification of catalytic activity and selectivity. For example, Liu and co-workers have theorized

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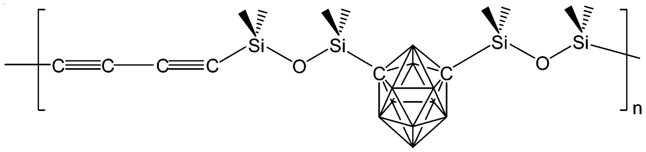
that the desulfurization of SO_2 and thiophene can have unexpected ligand and steric effects when performed on nanoparticles of Mo_2C instead of larger surfaces.[11] Hyeon and co-workers recently demonstrated the sonochemical synthesis of Mo_2C nanoparticles which exhibited dehydrogenation activity that was comparable to a dispersed Pt catalyst.[12] Nanoparticles of Mo_2C could also possess interesting electronic properties, as the bulk conducting and magnetic properties of nanoparticles are expected to be modified owing to the so-called quantum confinement effects.[13] Reported examples for the production of Mo_2C *nanoparticles* have utilized sonochemical,[12] CVD,[14] carbothermal hydrogen reduction,[15] and reactive-layer assisted deposition methods[16] as their means for production. The development of an organometallic pyrolysis reaction route for the production of the *nanoparticles* of Mo_2C is of great interest.

Chart 1. Diacetylene-Containing Carboranylenesiloxane, Poly(*m*-carborane-disiloxane-diacetylene) Used in This Study[a]



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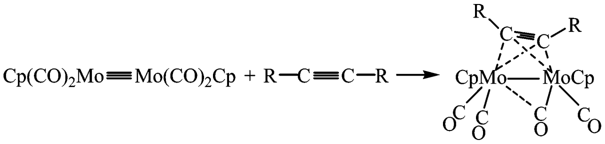
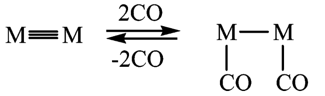
[a] The boron atoms occupy the vertices of the carborane cage.

Mo-containing organometallic complexes or polymers that are thermally stable are suitable precursors for exploring a pyrolysis reaction route for the production of Mo_2C nanoparticles. The reported examples of pyrolytic conversions of organometallic complexes to Mo_2C generate low yields of the material in its amorphous form.[17] Diacetylene-cross-linked carboranylenesiloxanes developed by Keller et al. are a group of materials that have excellent thermal and thermo-oxidative properties.[18] These materials can be converted into robust ceramics in high yield by pyrolysis to elevated temperatures of the networked system that forms upon the thermal cross-linking of the diacetylene units.[18] This propensity of the diacetylene-cross-linked carboranylenesiloxanes for ceramic formation by thermal means suggested that these materials could be suitable for conversion into metallic borides, carbides, or silicides, which require high reaction temperatures for their formations. The metal, in principle, could be incorporated within the polymer chain or as a part of a pendant group on the chain. On pyrolysis, a metal-incorporated diacetylene-containing carboranylenesiloxane such as **1** (Chart 1) would initially produce a cross-linked network, which could then be converted into the metal carbide, boride, or silicide, or their mixtures. Whether the metal-boride, -carbide, or -silicide was formed would be dictated by the proximity of the respective reactant atoms in the metal-derived polymer and the enthalpies and entropies of formation of the possible products. The incorporation of metal species in the polymer backbone of diacetylene-containing carboranylenesiloxanes has been amply demonstrated by Keller et al.[19] However, the functionalization of the polymer backbone in these polymers with metal units, as a part of a pendant group, has not been previously explored. The constituent diacetylene unit, prior to cross-linking, is an excellent candidate for metal incorporation since it is known to form adducts with various metal species using its individual acetylene (alkyne) units.[20] In fact, under photochemical conditions, some metal complexes are known to function as catalysts for the cross-linking of acetylenes and diacetylenes.[21] It has been well-established that alkynes in general add across the metal−metal triple bond in $Cp_2Mo_2(CO)_4$ to form adducts of the type $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}R{-}C{\equiv}C{-}R)$ with a tetrahedral C_2Mo_2 core (eq 1).[22] The triply bonded $Cp_2Mo_2(CO)_4$ has been reported to be generated from the singly bonded $Cp_2Mo_2(CO)_6$ by the elimination of two of its carbon monoxide ligands during a reflux of the latter in *m*-xylene for several hours (eq 2).[23] Hence, in this study, $Cp_2Mo_2(CO)_6$ was chosen as the reactant for the in situ production of $Cp_2Mo_2(CO)_4$ to explore its reaction with the diacetylene units in **1**, leading possibly to the formation of Mo_2C. In this paper, the organometallic reaction between **1** and $Cp_2Mo_2(CO)_6$, and the structural, macroscopic, and superconducting properties of the pyrolysis (800−1000 °C) residue of the reaction product are discussed.



$$\mathrm{Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp + R{-}C{\equiv}C{-}R \longrightarrow \underset{\mathrm{OC\;\,CO\qquad CO\;\,CO}}{\overset{\mathrm{R{-}C{\equiv}C{-}R}}{\mathrm{CpMo{-}MoCp}}}} \tag{1}$$



$$\mathrm{M{\equiv}M} \underset{-2\mathrm{CO}}{\overset{2\mathrm{CO}}{\rightleftharpoons}} \underset{\mathrm{CO}}{\mathrm{M}}{-}\underset{\mathrm{CO}}{\mathrm{M}} \tag{2}$$

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Experimental Section

Materials. All synthetic procedures were performed under a flow of argon using Schlenk line techniques. The diacetylene-containing carboranylenesiloxane, **1**, was synthesized according to a published procedure.[18a] $Cp_2Mo_2(CO)_6$ (98%, Strem) and tetrahydrofuran (THF, anhydrous, 99.9%, Aldrich) were used as received.

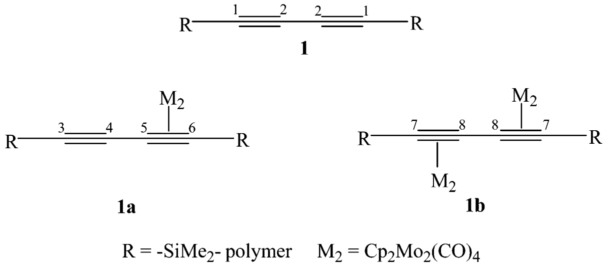
Instrumentation. Thermogravimetric analyses (TGA) were performed on viscous materials using a SDT 2960 DTA-TGA analyzer under a nitrogen flow rate of 100 cm^3/min. The heating rate was either 2 or 1 °C/min and the cooling rate was 5 °C/min. Infrared (IR) spectra were obtained as films on NaCl plates or as KBR pellets using a Nicolet Magna 750 Fourier transform infrared spectrometer. ^{13}C NMR spectra in $CDCl_3$ solvent were obtained using a 300 MHz Bruker Avance 300 NMR instrument (^{13}C @ 75 MHz). X-ray analyses were performed using a Rigaku 18 kW X-ray generator and a high-resolution powder diffractometer. X-ray diffraction scans of the samples were measured using Cu Kα radiation from a rotating anode X-ray source. The peak fit analysis of the diffraction data was conducted by fitting the diffraction profile with a Gaussian distribution function. The temperature-dependent dc resistivity measurements were carried out using a standard four-point probe configuration with the sample being slowly lowered into a liquid helium Dewar container. The resistivity value was estimated assuming that the sample was homogeneous and dense and thus should not be taken to be the true bulk value. For TEM analysis, a pulverized powdered sample was added to ethyl alcohol and the mixture was placed in an ultrasonic cleaner for 5 min. A carbon-coated 200 mesh copper grid was immersed in the mixture to pick up the nano-powdered samples. The specimen was examined in a Philips CM30 microscope operated at 300 kV.

Reaction of $Cp_2Mo_2(CO)_6$ with 1. A Schlenk flask, flame-dried under vacuum, was charged with 0.250 g (0.550 mmol) of **1** and 5 mL of THF under argon. In another flame-dried Schlenk flask, $Cp_2Mo_2(CO)_6$ (0.269 g; 0.550 mmol) was dissolved in 5 mL of THF under argon and the solution was cannulated into the former flask. The solution at this point had a blood-red appearance. The mixture was refluxed in an oil bath for 15 h. The solvent was then removed under vacuum to afford a wine-red product in quantitative yield (0.489 g; 99.9%). Spectroscopic data of the wine-red product: ^1H NMR (300 MHz, $CDCl_3$) (For product labels and atom notations, refer to Chart 2): δ 5.68 (s, C_5H_5, **1a**), 5.32 (s, C_5H_5, **1b**), 3.5−1.5 (br, $-CB_{10}H_{10}C-$), 0.30, 0.26, 0.20, 0.11, and 0.09 (s, $-Si(CH_3)_2-$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 241.5 (*C*O) (**1b**), 234.1(*C*O) (**1b**), 229.8 (*C*O) (**1b**), 226.5 (*C*O) (**1a**), 223.9 (*C*O) (**1a**); 132.46 (*C*4), 130.86 (*C*8), 128.79 (*C*5), 111.22 (*C*3), 95.72 (C_5H_5, **1a**), 92.29 (*C*6 and *C*7), 91.99 (C_5H_5, **1b**), 87.04 (*C*2), 84.85 (*C*1), 68.46, 68.14, 68.06, and 68.00 ($CB_{10}H_{10}C$), 1.80, 1.00, 0.47, and 0.28 ($-Si(CH_3)_2-$). IR (NaCl): $3113.76_{(\nu C-H)}$ (C_5H_5), $2962.07_{(\nu C-H)}$, $2598.78_{(\nu B-H)}$, $2070.44_{(\nu C-C)}$ (diacetylene), $1951.67_{(\nu C-O)}$, $1922.76_{(\nu C-O)}$, $1901.02_{(\nu C-O)}$, $1888.34_{(\nu C-O)}$, $1421.12_{(\nu C-C)}$, $1257.45_{(\nu Si-C)}$, $1081.80_{(\nu Si-O-Si)}$, $822.31_{(\nu Si-C)}$, $798.36_{(\nu Si-C)}$, 586.78, 554.84, 502.94.

Production of the Superconducting Mixture Containing Nanoparticles of β-Mo_2C. *(a) Cross-linking of the Wine-Red Reaction Product.* A portion (0.095 g) of the wine-red product, placed in a ceramic crucible, was heated in the TGA instrument under nitrogen to 250 °C at a heating rate of 2 °C/min and was held at this temperature for 30 min. Subsequently, the sample was heated to 400 °C at 2 °C/min and was held at this temperature for 120 min. The cross-linked networked product was then cooled at 10 °C/min to room temperature affording a weight retention of 66%.

(b) Thermal Reaction of the Cross-linked Networked Product. The cross-linked networked product (0.062 g), obtained from (a), was heated to 1000 °C in a ceramic crucible in a TGA instrument under nitrogen in two steps. It was first heated to 400 °C at 2 °C/min and subsequently to 1000 °C at 1 °C/min. The material was then cooled to ambient temperature at 5 °C/min affording a char yield of 89%.

Chart 2. Possible Products (1 (with Unreacted Diacetylene Units), 1a (with Partially Reacted Diacetylene Units), and 1b (with Completely Reacted Diacetylene Units)) in the Reaction between 1 and $Cp_2Mo_2(CO)_6$ with Notated Carbon Atoms of the Diacetylene Units



Results and Discussion

The selection of THF as the reaction solvent in the current study was made to facilitate the displacement of the carbonyl ligands in $Cp_2Mo_2(CO)_6$ by the diacetylene units in **1**. $Cp_2Mo_2(CO)_6$ is known to exist in solution as a mixture of trans and gauche isomers.[24] In most solvents, the predominant isomer is trans. In solvents such as DMSO, THF, DMF, or mixtures of them the ratio can be reversed.[25] Between the trans and gauche isomers, the carbonyl exchange or displacement with the lowest energy dynamics is observed in *gauche*-$Cp_2Mo_2(CO)_6$.[25] The amount of $Cp_2Mo_2(CO)_6$ that was reacted with **1** was chosen so as to spare free acetylene moieties in **1**, either as a free acetylene fragment in a partially reacted diacetylene unit or as an unreacted diacetylene unit, after the reaction. Thus, unreacted diacetylene units or acetylene fragments in the product would be available for further conversion of the product into networked systems by thermal treatments. In a reaction performed at an equimolar ratio of **1** and $Cp_2Mo_2(CO)_6$, the three products **1**, **1a**, and **1b** (Chart 2**)** are expected to be formed in various amounts depending on the reaction kinetics. In this study, the evidence of the reaction and its progress was provided by FTIR spectroscopy. The equimolar reaction of $Cp_2Mo_2(CO)_6$ with **1** in refluxing THF resulted in the displacement of two of its carbonyl ligands by the diacetylene units in **1**, yielding the transient, reactive triply bonded $Cp_2Mo_2(CO)_4$ and, subsequently, its π-bonded complex with **1**. As the reaction progressed, the initial IR absorptions of $Cp_2Mo_2(CO)_6$ (1960 and 1915 cm^{-1}) were replaced by new IR absorptions at 1950, 1923, 1900, and 1891 cm^{-1} of the diacetylene-bound $Cp_2Mo_2(CO)_4$ moieties (Figure 1). The presence of an unchanged diacetylene absorption at 2070 cm^{-1} in the FTIR spectrum of the final product suggested that a fraction of the starting material **1** had remained unreacted as expected. Since the reaction was quantitative in yield, this implied that the starting reactant $Cp_2Mo_2(CO)_6$ had to be distributed among the reacted fraction of **1** yielding

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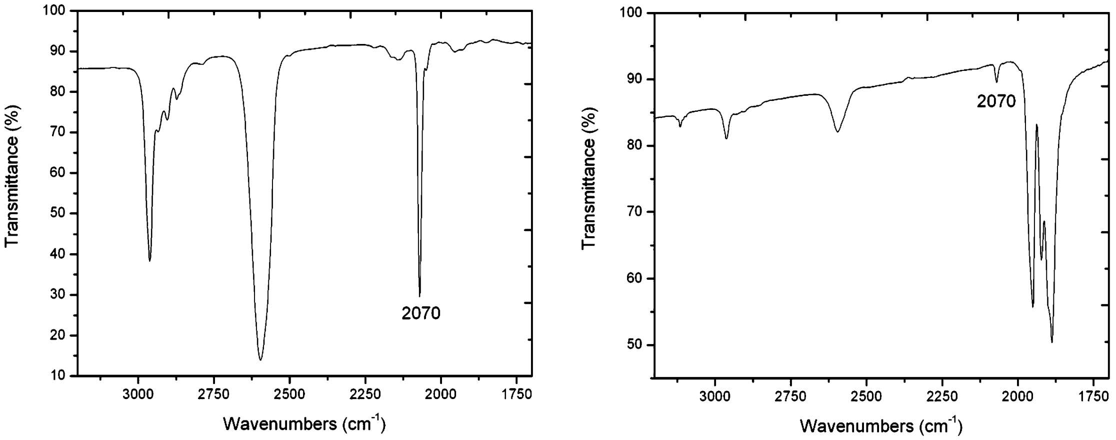

Figure 1. FTIR spectra of **1** (left) and the product from the reaction between **1** and $Cp_2Mo_2(CO)_6$ (right).

either a mono- or a bis-π-coordinated η^5-cyclopentadienyltetracarbonyldimolybdenum complex. Such a formation of π-complexes has been reported in the reaction involving $Cp_2Mo_2(CO)_4$ and the conjugated enediyne, *E*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene.[26] Further evidence for the retention of a fraction of **1** in its unreacted form was obtained from the product's ^{13}C NMR spectrum in $CDCl_3$. In the ^{13}C NMR spectrum, the NMR resonances of the diacetylene carbons (C1 and C2; Chart 2) of **1** at δ 87.05 and 84.81 were still evident, indicating the presence of some unreacted **1**. In addition, the resonances for the carbons of the diacetylene units in the mono- and bis-$Cp_2Mo_2(CO)_4$ derivatives of **1** (Chart 2) were observed at δ 132.46 (C4), 130.86 (C8), 128.79(C5), 111.22 (C3), and 92.29 (C6 and C7). Unique resonances were also observed for the cyclopentadienyl groups (δ 95.72 (**1a**); δ 91.99 (**1b**)) and the carbonyl ligands (δ 241.5 (**1a**), 234.1 (**1a**), 229.8 (**1a**); 226.5 (**1b**), 223.9 (**1b**)) of the π-coordinated mono- and bis-$Cp_2Mo_2(CO)_4$ complexes. The observed ^{13}C resonances are well in agreement with similar reported values for the π-coordinated mono- and bis-$Cp_2Mo_2(CO)_4$ complexes formed from the reaction between $Cp_2Mo_2(CO)_4$ and the conjugated enediyne, *E*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene.[26] The FTIR and FTNMR spectroscopic studies of the reaction product confirmed that free diacetylene units and acetylene fragments were available in the product for its conversion into a network system by thermal cross-linking. The cross-linking (curing) was achieved by the thermal treatment of the product to 400 °C in two steps of various durations. On cross-linking, the strands of the oligomers with the partially or completely functionalized diacetylene units were expected to be bound within a tightly cross-linked network system formed by the thermal polymerization of the diacetylene units (in the unreacted **1**) and the acetylene fragments (in the partially reacted **1**). A tightly cross-linked network was expected to enhance the entrapment of the reactant moieties in closer proximity during the initial stage of the pyrolysis, thereby facilitating product formation. The pyrolysis of the cross-linked network was achieved by the thermal treatment of the network to an elevated temperature (1000 °C), which resulted in the conversion of the matrix to the eventual products. Weight losses during the initial curing and the subsequent pyrolysis of the cross-linked network were 33% and 11%, respectively. These losses corresponded roughly to the elimination of the labile carbonyl and cyclopentadienyl ligands during the initial curing process and the subsequent expulsion of the silicon-bound methyl groups during the later stages of the curing process and during pyrolysis. The deletion of carbonyls and cyclopentadienyl rings from organometallics has been known to occur at temperatures below 300 °C.[27] The loss of methyl groups from siloxyl units has been reported to occur in the 450−550 °C temperature range.[28] To ascertain the assumptions of the respective losses of ligands from the cross-linked network, a TGA-DTA thermogram of the network was obtained by thermally treating it to 1000 °C at 10 °C/min (Figure 2). As seen in Figure 2, the differential curve in the thermogram exhibits two sharper peaks (transitions) around 222 and 267 °C and a broader peak centering at 525 °C. The sharper peaks represent the successive removal of the carbonyl and the cyclopentadienyl ligands within a narrow temperature range and the latter broad peak originates from the removal of the silicon-bound methyl groups over a large temperature range. Further evidence for the respective removal of the ligands during the cross-linking of the reaction product between **1**

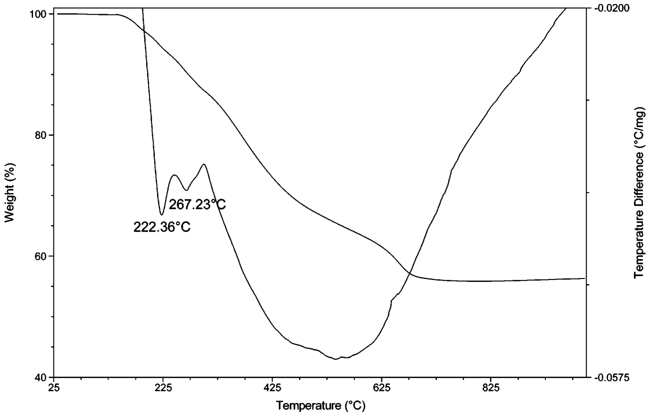

Figure 2. TGA-DTA thermogram of the product from the reaction between **1** and $Cp_2Mo_2(CO)_6$ during its thermal treatment to 1000 °C. (Heating rate = 10 °C/ min).

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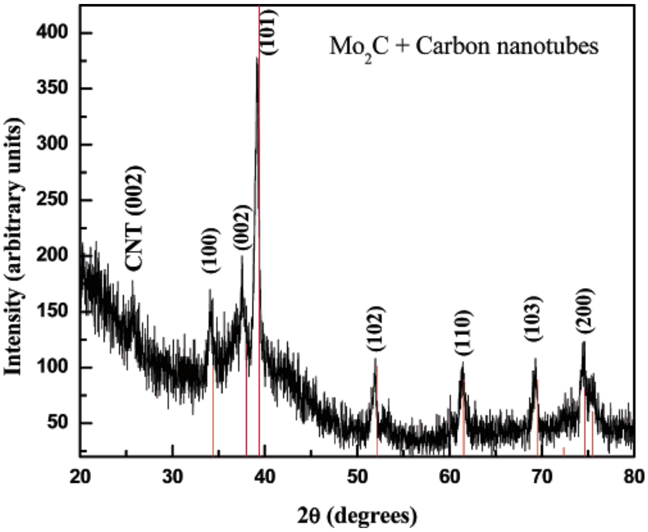

Figure 3. XRD spectrum of the pyrolysis product of the $Cp_2Mo_2(CO)_4$ complex of **1**.

and $Cp_2Mo_2(CO)_6$ were also obtained from the solid-state FTIR spectra (in KBR pellets) of cross-linked samples obtained by the thermal treatment of the reaction product at 300 °C (for 1 h) and 550 °C (for 2 h), respectively. In the FTIR spectrum of the former, the IR absorptions of the carbonyls (1950, 1923, 1900, and 1891 cm^{-1}) and that of the cyclopentadienyl ligands (3114 cm^{-1}) in the reaction product were found to be absent, while in the latter's FTIR spectrum in addition to the carbonyl and cyclopentadienyl absorptions, the absorptions for the silicon-bound methyl groups (1257, 822 cm^{-1}, etc.) were also absent.

The identity of the pyrolysis product was ascertained by an X-ray diffraction analysis of the pyrolysis char. The X-ray diffraction spectrum of the char revealed the presence of Mo_2C possessing a hexagonal space symmetry (Figure 3) along with a small amount of carbon nanotubes. The diffraction pattern consists of eight distinct lines which are all assigned to β-Mo_2C based on an excellent fitting with literature data (JCPDS 35-0787).[29] The peak for the carbon in the carbon nanotubes was evident at $2\theta = 25.9°$. A fundamental question that is central to this study was whether all of the molybdenum units existed as β-Mo_2C or whether only a small fraction of the molybdenum units were in their β-Mo_2C form with the rest of molybdenum units being present as their compounds of silicon and/or boron. The broad baseline in the diffraction spectrum around the peak at $2\theta = 39°$ indicated that a fraction of the molybdenum units existed in the pyrolized mixture as its compounds of silicon and/or boron. The peak fit analysis of the diffraction data suggested that the integrated intensity of the amorphous peak around 39° in 2θ was about 20% of the overall integrated intensities of the crystalline peaks of the Mo_2C phase. The diffraction profile was fitted with a Gaussian distribution function. Based on the peak fit analysis, it is estimated that in the pyrolysis product the amorphous molybdenum compounds exist up to an upper limit of 20%. Hence, the pyrolysis predominantly yields molybdenum in its β-Mo_2C form. The preferential formation of crystalline β-Mo_2C during the pyrolysis could be attributed to the favorable crystallization energy of β-Mo_2C under the pyrolysis conditions when compared to other possible molybdenum products (with silicon and/or boron). It is possible that, at conducive conditions for nucleation and growth, other crystalline molybdenum compounds of silicon or boron could be obtained from this system in preference to β-Mo_2C. In the amorphous fraction of the pyrolized residue, the formation of ternary amorphous alloys involving molybdenum, silicon, and boron during the pyrolysis cannot be discounted, although the formation of such alloys has only been reported during melt or liquid quenching of pure mixtures of molybdenum, silicon, and boron[30,31] or from arc melting of the pure materials under argon at a low temperature.[32,33] For example, the generation of a ternary alloy such as Mo_5SiB_2 requires the arc melting of pure materials Mo (99.97%), B (99.5%), and Si (99.995%) in a cooled copper crucible under pure argon (99.998%).[33] The absence of such rigorous reaction conditions possibly rules out the formation of a ternary Mo−Si−B alloy in the current pyrolysis reaction.

The carbon nanotubes formed during the pyrolysis presumably originated from the catalytic interaction of Mo atoms, clusters, or nanoparticles with the diacetylene carbons since the remaining carbon sources were not observed to have survived a temperature above 600 °C as indicated by the TGA-DTA thermogram of the reaction product. It is well-known that binary transition metal catalysts containing molybdenum such as Co−Mo or Fe−Mo catalyze the formation of single wall carbon nanotubes by the CVD method from a carbon feedstock (e.g., hydrocarbon or CO).[34] Co or Fe in the binary catalyst is known to be the active participant in the nanotube formation with Mo acting as a cooperatively activity-enhancing supporting species. Co or Fe in such systems is gradually reduced to the metal whereas Mo is transformed to its carbide (Mo_2C). However, there are very few examples of molybdenum acting as a sole metal catalyst for the production of carbon nanotubes.[35]

The production of both Mo_2C and carbon nanotubes on pyrolysis of the $Cp_2Mo_2(CO)_4$ complex of **1** was further confirmed by TEM analysis of the pyrolysis char (Figure 4). The fibrous networks of the carbon nanotubes in the char were clearly observed in the TEM micrographs along with the hexagonal nanoparticles of β-Mo_2C. The veinlike carbon nanotubes stretch to several micrometers as seen from the TEM micrographs. The sizes of the β-Mo_2C nanoparticles were in the range of 30−80 nm, with a few of the particles being larger than 100 nm. Together, the XRD and TEM data

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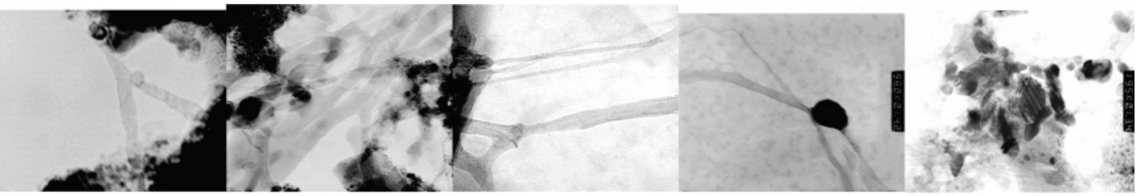

Figure 4. TEM micrographs of the pyrolysis product of the $Cp_2Mo_2(CO)_4$ complex of **1**.

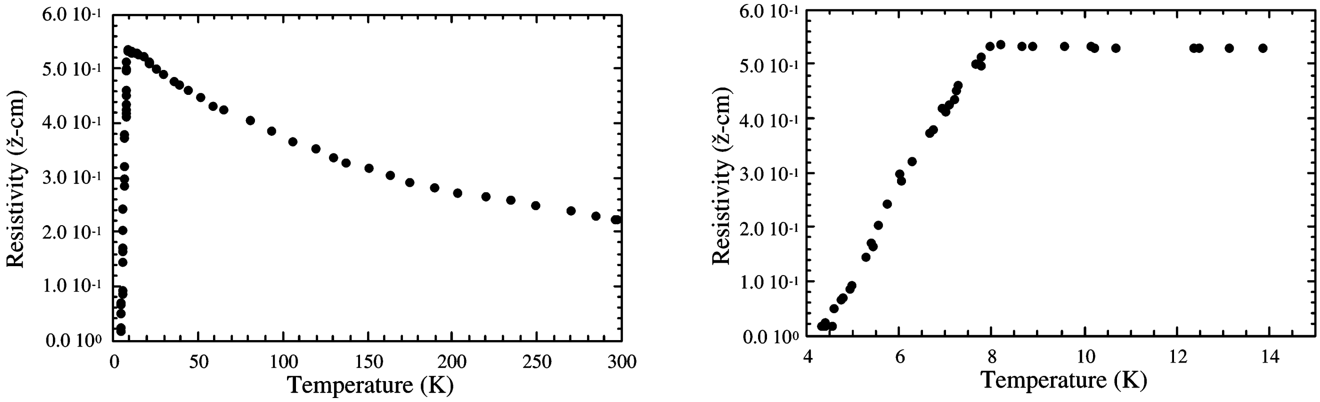

Figure 5. Resistivity plot of the pyrolysis product of the $Cp_2Mo_2(CO)_4$ complex of **1**.

unequivocally confirm the formation of β-Mo_2C in nanometric dimensions along with some carbon nanotubes.

The resistivity measurement of the pyrolysis residue containing nanoparticles of β-Mo_2C was of interest to determine whether there was any significant alteration in the conducting properties of β-Mo_2C in its nanoparticle form when compared to its reported conducting properties in the bulk form.[1] The measurement was made with the understanding that the observed value of the conductivity of the pyrolysis residue would be an additive function of the contributions to the conductivity by the individual components (β-Mo_2C, carbon nanotubes, and about 20% of amorphous molybdenum compounds of silicon and boron) in the char. A distribution of this value into individual contributions would be impossible unless the components were separated and their conductivities measured individually. The measurement was also made with the appreciation that the size effects of materials on superconductivity are theorized to be observed only in the realms of 2−5 nm particle sizes and below.[36] Resistivity measurements on the pyrolysis residue showed a broad superconductive transition beginning at 8 K and with $\rho = 0$ below 4 K, which is the lowest temperature achieved (Figure 5). This broad transition is likely due to the granular, inhomogeneous nature of the sample. The two obvious candidates for superconductivity in the pyrolyzed residue are β-Mo_2C and carbon nanotubes. While superconductivity in Mo_2C was reported long ago,[1] the discovery of superconductivity in ropes of single-walled carbon nanotubes[37] is more recent. An amorphous molybdenum−silicon−boron ternary alloy is a possible third candidate, provided it is formed. Superconductivity has been observed in Mo−Si−B ternary amorphous alloys formed by solid or melt quenching processes.[30,31] A comparison of the observed onset temperature (8 K) of the residue with the reported T_c values of the three candidates shed some light on the most probable candidate for the observed superconductivity. The T_c value of 8 K for the pyrolysis residue is higher than that reported by Morton et al. for hexagonal β-Mo_2C produced from sintered molybdenum wires (5.1−5.7 K) or from vapor-deposited samples (6.3−7.2 K) and for α-Mo_2C (6.7−7.3 K).[38] These T_c determinations had replaced the then existing values for α-Mo_2C (4 K)[39] and β-Mo_2C (2.4−3.2 K[1b] or 2.78 K[40]). The α-Mo_2C and β-Mo_2C used in the then existing determinations were found to have had significantly lower stoichiometric composition of carbon in the lattices and thus lower carbon concentrations. The observed onset temperature of the residue is in the temperature range (8.1−12.2 K) reported for hexagonal β-Mo_2C with a perfect stoichiometric composition, which had further refined the results of Morton et al.[41] This positions β-Mo_2C as a strong contender for superconductivity in the pyrolysis residue. The onset temperature is also very close to the T_c values of known Mo−Si−B ternary amorphous alloys. Mo−Si−B ternary amorphous alloy ribbons with a composition $Mo_{70}Si_{20}B_{10}$ prepared by a liquid quenching method have been reported to have a T_c of ~6.8 K.[30] Additionally, the superconducting temperature of the amorphous molybdenum−silicon−boron ternary amorphous alloys with a composition $Mo_{70-77.5}Si_{7.5-20}B_{7.5-20}$ obtained by melt quenching has been determined to be between 5.7 and 7.1 K, increasing with a decreasing amount of combined Si

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and B mass and with increasing replacement of Si by B.[31] Thus, a Mo−Si−B ternary alloy could also have been responsible for the observed superconductivity in the pyrolyzed residue. However, as previously described, the absence of very rigorous reaction conditions possibly rules out the formation of a ternary Mo−Si−B alloy and its role in the genesis of superconductivity in the pyrolytic residue. A comparison of the T_c value of the pyrolyzed residue to that of the reported values for ropes of carbon nanotubes reveals that it is quite unlikely that the generated carbon nanotubes are solely responsible for the superconductivity. To date, the T_c values reported for various samples of ropes of SWNT are below 1 K.[37] Additionally, superconductivity in carbon nanotubes is observed only when their lengths are greater than the coherence length, ξ, thereby limiting superconductivity to long ropes of carbon nanotubes.[42] A more detailed characterization of the carbon nanotubes produced in the current study should determine whether they have the necessary characteristics for exhibiting superconductivity. In the event that the carbon nanotubes formed in the pyrolysis residue are superconducting, the possibility that they have had an effect on the observed onset temperature of the mixture cannot be discounted. Thus, as expected, the experimental data from resistivity measurements of the pyrolysis residue suggest that the size range (30−80 nm) of the nanoparticles of β-Mo_2C produced in the current study is not small enough to have caused substantial changes in the reported conductivity of β-Mo_2C assuming that the superconductivity in the pyrolysis residue arose solely from β-Mo_2C nanoparticles. Further studies are underway to clarify this aspect and thereby to unambiguously determine the identity of the superconducting component.

Conclusions

The utility of the thermo-oxidatively stable diacetylene-containing carboranylenesiloxane, **1**, as a viable system for the formation of *nanoparticles* of the transition metal carbide Mo_2C has been demonstrated in the current study. In line with its intent, efforts are underway to separate the β-Mo_2C nanoparticles from the generated mixture. The separated β-Mo_2C nanoparticles, carbon nanotubes, and other components should lend themselves to thorough characterizations of their conducting properties. Such determinations should be interesting as they should reveal whether any component other than β-Mo_2C is responsible for the observed superconducting characteristics of the pyrolysis residue. The separated nanoparticles of β-Mo_2C will also be utilized as a catalyst in reactions such as hydrodesulfurization and dehydrogenation to study the effect of the generated β-Mo_2C nanoparticles' size on their efficiency and on the selectivity of the reaction products. More importantly, this study has demonstrated that the diacetylene-containing carboranylenesiloxane **1** has the ability to react readily with a metal compound possessing the ability to form a π-complex with its diacetylenic units to provide mono- and bis-π-coordinated complexes. This opens an avenue for the incorporation of a vast group of metals (either singly or in a mixed fashion) in **1** by utilizing the reactions of their complexes containing labile ligands such as CO, COD, and CN with **1**. In addition to the established "in-chain" metal incorporation, this avenue for the incorporation of metal units as a part of pendant groups on the polymer chain enhances further the possibility for the fine-tuning of reaction dynamics and, thus, of the products from the pyrolytic reactions of metal-derived polymers of **1**. The possibility for further fine-tuning also exists by the predetermination of the fraction of the diacetylene units in **1** that is to be reacted with the metal units and by controlling the rate and the temperature of the thermal treatment during the pyrolysis reactions. In summary, a plethora of possible metal-derived complexes of **1** resulting from diacetylene functionalizations should afford the opportunity to produce nanomaterials of various metal carbides, borides, silicides, etc., with diverse conducting, magnetic, and catalytic properties.

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