Perforated organometallic nanotubes prepared from a Rh N-heterocyclic carbene using a porous alumina membrane

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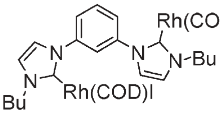
Fabrication of perforated organometallic nanotubes using a dirhodium bis(N-heterocyclic carbene) complex by a simple nanoporous template wetting technique is described along with characterization data from scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), proton NMR and Mass spectroscopy.

Many groups world-wide are involved in the development of nanotubes.[1,2] The ubiquitous carbon nanotubes receive much attention.[3] The fabrication of nanotubes from polymers *via* a templating methodology has been reported recently.[4] Nanotubes have been demonstrated to have potential application for hydrogen storage and fuel cell technology.[5] Despite these large scale synthetic efforts very few examples of organometallic nanotubes have been reported.[6] We report the preparation of nanotubes from an organometallic material based on the porous alumina membrane templating methodology. Furthermore, the organometallic nanotubes contain semi-regular perforations (pores) along the main axis of the tube. This highly desirable property opens the possibility of controlled drug delivery with biocompatible metals and many other applications.[7]

The construction of nanotubes, especially single-walled carbon nanotubes (SWNTs), has focused on solid walled materials. In part this is driven by the applications that have been envisaged and the available methodologies. Much has been reported concerning defects (holes) in the walls of SWCNTs and their spherical counter part C_{60}.[8,9] Solid-walled nanotubes are the microscopic counterparts to rigid PVC pipe. An alternative macroscopic model is perforated pipe, which has regularly spaced pores that serve many functions.

The orange, crystalline di-Rh bis(N-heterocyclic) carbene (NHC) complex **1** depicted below was recently reported by two of us.[10] The potential for crosslinking the Rh centers into a polymeric array made them interesting potential starting materials for nanotube synthesis. The nanotubes were fabricated by wetting a porous alumina membrane template with a toluene solution of **1** and allowing the solution to permeate the membrane until it was saturated.[4a,11] The solvent was allowed to evaporate under ambient conditions. The excess precipitate was removed from the surface of the membrane, and the alumina was dissolved with 3 N NaOH followed by centrifugation. The aqueous supernatant was discarded and a yellow solid was isolated. This material was rinsed with water and dried at room temperature.†



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Preliminary identification of the morphology was conducted by optical microscopy after dissolving the template but before resuspension and washing (Fig. 1). Bunches of aligned strands or fibers were noted as may be seen in Fig. 1. The alignment of the nanotubes is a simple consequence of the structure of the porous alumina membrane. Individual nanotubes appeared to be about 20 μm in length.

The structure and constitution of these nanotubes were addressed first. Samples for scanning electron microscopy (SEM) were prepared and immediately imaged for morphological information and for quantitative length and diameter measurements (Fig. 2). No gold coating was used for the SEM sample preparation and yet the imaging was free from any charge build-up. This fact is indirect evidence that the nanotubes may be conductive. Fig. 2 shows images of these tubes with pores at regular intervals. The regularity is so astonishing that it causes doubt that these are due to the surface profile of the alumina template. Many groups around the world have used porous alumina membranes for the fabrication of nanomaterials but there are no similar reports in the literature that indicate perforation features on the nanotubes such as those observed in our case. Therefore, we suggest that the pores are due to the nature of the

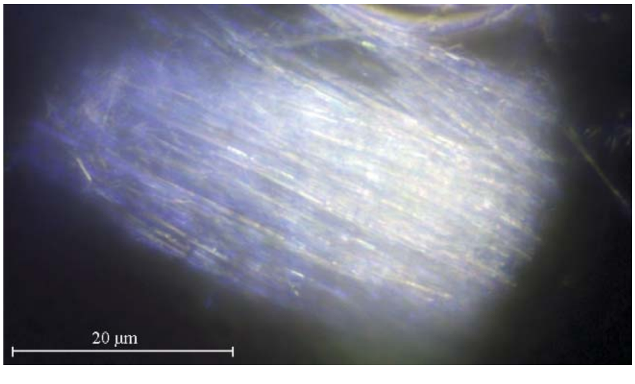

Fig. 1 Optical images at 1000× magnification illustrating the nature of and alignment of the fibers obtained initially.

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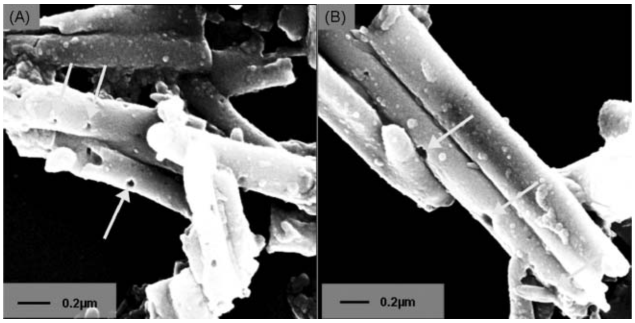

Fig. 2 Scanning electron micrographs of perforated organometallic nanotubes. Length 3–10 μm, width 200–250 nm. Regular perforations are observable along the length of several examples. Arrows indicate the perforations.

organometallic precursor and the type of bonding involved in creating the tubes. Our working hypothesis is that the NaOH removes a localized chemical structure that occurs periodically in the nanotube structure.

We have conducted transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) to understand further the physical features and the constitution of the nanotube structure. The TEM studies (Fig. 3) supported the nanotube SEM images. TEM images of the nanotubes dispersed on a lacey carbon coated Cu TEM grid are presented in Fig. 3. The lack of contrast down the center of the tubes (Fig. 3A) indicates the nanomaterial to be hollow. The wall thickness ranges from 40–60 nm. We observed shorter lengths in the SEM and TEM images than by optical microscopy and attribute the change to centrifugation and re-suspension, which may be shortening the tubes. The regularly spaced nanopores (perforations) are also evident in Fig. 3 (arrows).

All X-ray diffraction experiments are consistent with an amorphous structure. The elemental composition of the nanotubes was characterized by EDS studies of single nanotubes, which supported the presence of the organometallic material by showing the corresponding peak for the elements: C, Rh, I and N (Fig. 4). The Cu signal is due to the matrix upon which the tubes are placed for analysis. Peaks due to Na and O are attributed at present to residual contaminants from the aqueous NaOH used to dissolve the porous alumina membrane. Re-dissolving the perforated organometallic nanotubes proved especially insightful in investigating the structure of the nanotube. A sample was subjected to anhydrous and acid-free $CDCl_3$ and gave a homogenous pale yellow-orange solution. A 500 MHz ^1H NMR spectrum of the re-dissolved material was collected and compared to that of **1**. Selected portions of the spectra are presented in Fig. 5 illustrating the recovery of the intact organometallic molecule **1**. The signals due to the methylene group attached to N of the butyl substituent is labeled * and the coordinated cyclooctadiene are labeled # in Fig. 5. Since "free" N-heterocyclic carbenes ($pK_a \sim 25$) are not stable in an aqueous environment (alumina removal with aqueous NaOH),[12] this experiment establishes that the Rh–NHC bond remains intact in the nanotube. Additionally, the molecular ion for $[M - I]^+$ ($m/z = 871$) from the re-dissolved sample was observed

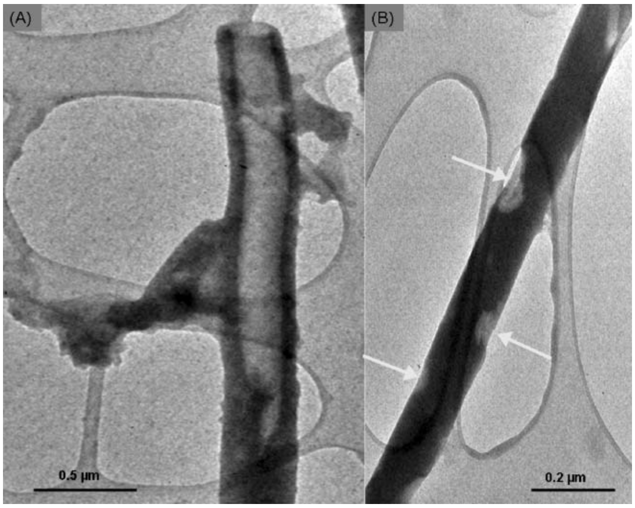

Fig. 3 Transmission electron microscopy of organometallic nanotubes illustrating the hollow nature of the tubes due to the observed translucence (A) and regularly occurring pores (B). Arrows indicate the perforations.

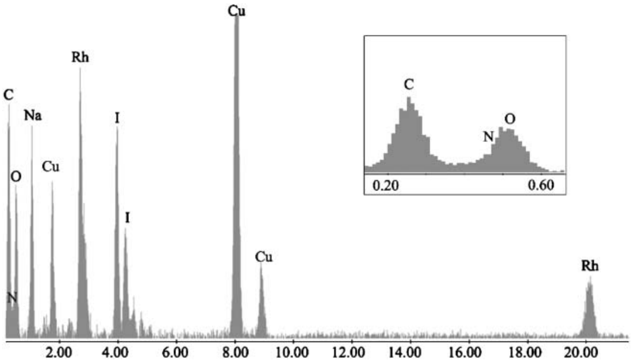

Fig. 4 Energy dispersive X-ray spectroscopy (EDS) of the nanotubes indicating the presence of constituent elements Rh, N, C, I. The large central peak is due to the Cu matrix used in the analysis.

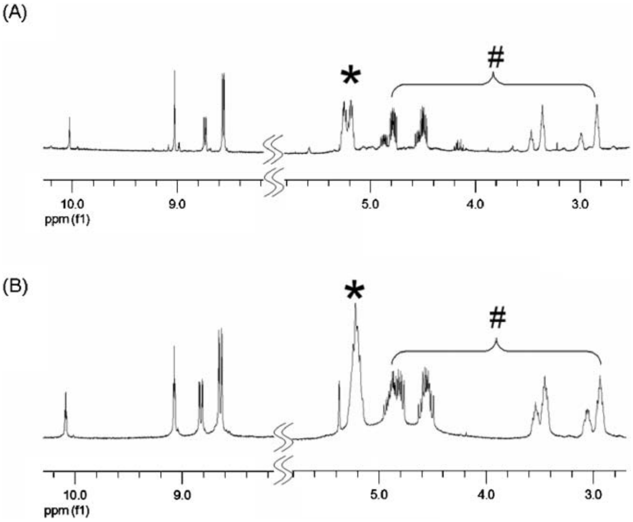

Fig. 5 A comparison of selected regions of the 500 MHz ^1H NMR spectrum of the re-dissolved nanotube material (A) demonstrating recovery of the intact molecule **1** and (B) the spectrum of the di-Rh bis(NHC) starting material collected in CD_2Cl_2. The methylene group of the Bu substituent is indicated by *. The signals due to coordinated cyclooctadiene (COD) are indicated with #.

by liquid secondary ion mass spectroscopy (LSIMS). An identical observation was made for the starting material **1**.[10]

These observations make even more intriguing the question of the nature of the molecular forces or non-covalent interactions holding the perforated organometallic nanotube together. There are several possible explanations. It could be intermolecular van der Waals attractions between butyl groups with or without concomitant π-stacking of the aromatic rings.[13] Alternatively, the porous alumina membrane may catalyze a ligand exchange process whereby Rh–I–Rh and/or Rh–cyclooctadiene–Rh bridges are formed.[14,15] The ready dissolution of the nanotubes in chloroform and the spectroscopic data (*vide supra*) seem to preclude the formation of μ-oxo (Rh–O–Rh)or μ-hydroxo (Rh–OH–Rh) bridges during treatment with NaOH.[16,17] The suggested explanations account for the ready solubility in chloroform and account for recovery of **1**.

In conclusion, we have fabricated nanotubes from a di-Rh N-heterocyclic carbene complex by a facile technique. These organometallic nanotubes seem to have good electrical conductive properties and show promise as nanowires. In addition, the presence of perforations (nanopores) at regular intervals in the nanotubes opens the possibility of numerous other applications. In the case of our nanotubes, the perforations around their sidewalls would make it easier for material to diffuse in and out of the tubes. Work is underway to ascertain the chemical structure of the tubes, to determine the molecular or non-covalent forces holding the tubes together, to insert objects into the tubes and to gain insight into the source of the perforations (nanopores), which will enhance our ability to control them.

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Notes and references

† *Experimental*: The 25 mm alumina disc templates with pore size of 200 nm were procured from Whatman Inc. The alumina template was sonicated for 10 min in deionised water to clean the pores and allowed to dry. Air and moisture stable di-Rh **1** (9.98 mg) was dissolved in toluene (5 mL). An aliquot of the solution was applied to the top of a template by microsyringe and the solvent allowed to evaporate overnight under a lamp in air. The excess solid was removed from the top of the template with a toluene dampened Kimwipe®. The template was dissolved with 3N NaOH (2 mL), the solid was centrifuged, and the supernatant was decanted. The nanotubes were washed twice by suspension in distilled H_2O followed by centrifugation and decantation. They were suspended in water and drop-cast onto a Si substrate and dried before analysis. Optical microscopy images were collected from a Nikon Eclipse E600. A Leo Supra 55 was used to collect the SEM images and a Philips CM300 was used to collect the TEM images and the EDS data. High resolution proton NMR data were recoded on a Varian Inova 500 MHz instrument.

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