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Application of heteroatom-containing iron(II) piano-stool complexes for the synthesis of shaped carbon nanomaterials



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ABSTRACT

Based on iron(II) piano-stool complexes, five compounds were synthesized by varying the organoheteroatom ligands in their structure. Two different heteroatoms were considered, namely, nitrogen and sulfur, as constituents of the ligands on the complexes. Compounds **1** and **2** contained the nitrogen heteroatom in their ligands whilst **3** to **5** contained sulfur. These compounds were used as catalysts in the synthesis of shaped carbon nanomaterials (SCNMs) by means of the floating catalyst chemical vapour deposition method (CVD). The nitrogen-containing catalysts produced nitrogen-doped carbon nanotubes (N-CNTs) with bamboo morphology. On the other hand, the sulfur-containing catalysts produced mainly carbon spheres (CS) and some amorphous carbon (AC) as the bulk of the resulting SCNM products. In the case of compounds **1** and **2**, higher nitrogen content and reaction temperatures were shown to promote nitrogen-doping which led to more disordered N-CNTs and an increase in the outer diameter of the N-CNTs. In the case of compounds **3** to **5**, higher reaction temperatures led to more graphitic CS and an increase in the average diameter of the CS. The various results and analyses show that the synthetic variations of not only reaction conditions, but also the type of substituent on the organometallic catalyst ligand and its structure, can lead to a level of control towards the resulting carbon nanostructures.

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Introduction

Shaped carbon nanomaterials (SCNMs) display interesting properties that are closely related to their shapes and sizes. Hollow or filled carbon spheres (CSs), carbon nanotubes (CNTs) and fullerenes, amongst other SCNMs, have been shown to have interesting properties and applications across most scientific and technological fields [1,2]. Some of the properties exhibited by SCNMs include high surface areas, which permit applicability in areas such as catalyst supports [3,4], gas adsorption [4,5] and water purification systems [6,7]. Whilst the formation mechanisms of SCNMs is still a fascinating phenomenon [8], the synthesis procedures require a certain level of control towards the desired products and their dimensions.

SCNMs can be synthesized by a variety of techniques which include chemical vapour deposition (CVD) [9], laser ablation [10] and arc discharge [11]. Amongst the three, CVD has proven to be the most facile method that can be made selective towards the production of a particular SCNM [12]. A greener CVD method that has been used involves the introduction of a catalyst and any other reactant/s into a closed environment (autoclave), which is then heated under autogeneous conditions. This technique avoids the use of a catalyst support and eliminates the related difficult and expensive support removal procedures [13].

The addition of heteroatoms during the synthesis of SCNMs by the CVD method is one way to improve the selectivity and yield towards specific SCNMs [14]. Depending on the heteroatom introduced, the carbons on the structure of the SCNMs can be replaced with the added heteroatom, as a dopant. This can be achieved by the addition of a heteroatom-containing carbon source, heteroatom-containing catalysts or a combination of both approaches.

The use of nitrogen-containing compounds has been shown to result in the incorporation of N-atoms and the production of nitrogen-doped CNTs (N-CNTs) [15–19]. N-CNTs display a "*bamboo-like*" morphology because of the disorder introduced by the nitrogen [17]. The extent or level of nitrogen-doping in N-CNTs is related to the distances (segmental length) of the bamboo compartments [18]. The nitrogen atom in N-CNTs may also serve as a functionalization point for the introduction of a number of other functional groups.



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Sulfur is another heteroatom that has been introduced during SCNM synthesis by means of the CVD method [20]. Unlike nitrogen, a dopant, sulfur has been reported to act as a promoter when introduced during the synthesis of SCNMs [21]. Hence, the sulfur atom is not incorporated into the structures of the SCNMs but has been shown to increase yields [14] and improve selectivity towards certain types of SCNMs [8,9]. For example, sulfur as an additive, has been known to introduce Y-shaped CNTs and aid in the formation of helical carbon nanotubes (HCNTs) [22]. In addition, the presence of sulfur, during the synthesis of SCNMs *via* the CVD method, has been shown to enhance the encapsulation of ferromagnetic moieties, thus improving the soft magnetic properties of the CNTs, making them suitable for applications in electromagnetic devices.

Owing to their volatile nature, organometallic compounds are commonly used as catalysts in the synthesis of SCNMs *via* the CVD method [23]. A good example of such organometallic compounds is iron pentacarbonyl, Fe(CO)₅, which has been successfully used to synthesize SCNMs [23]. The use of polymers containing organometallic complexes to provide a metal source for CNT synthesis has also been reported to yield a controlled production of CNTs [24,25]. However, there is need to explore a wider scope of catalysts to deepen the understanding of catalyst structure-product property relationships. In the past, we have synthetically modified ferrocene to incorporate a variety of ligands that alter the catalyst properties and thus alter the properties of resulting SCNMs [19,26,27]. Incorporation of heteroatoms directly into the ligands of the catalyst has also been shown to be a more effective way of modifying the SCNMs produced compared to their introduction as external dopants [28].

Our current focus is on the use of iron(II) piano-stool complexes as catalysts for the synthesis of CNTs and other SCNMs. An initial report from Mohlala et al. has described the synthesis of pristine multi-walled CNTs by using iron(II) piano-stools [29]. However, we are now introducing more variable heteroatoms within the catalyst and exploring the kind and properties of SCNMs obtained at different conditions.

In this study we report the synthesis of five iron(II) piano-stool complexes and their use as catalysts for the synthesis of SCNMs *via* the CVD method. The first two compounds possess ligands functionalized by nitrogen and oxygen heteroatoms with different structures and amounts of nitrogen and oxygen. Hence, it would be interesting to investigate how these two iron(II) piano-stool complexes will affect the level of nitrogen-doping in the resulting SCNMs. The other three compounds contain the sulfur-heteroatom incorporated in different chain lengths as ligands. These are also explored to establish how the presence of sulfur and varying the ligand chain length affects the yields, morphology and selectivity towards the SCNMs produced.

Results and discussion

Synthesis of iron(II) piano-stool complexes

The synthesis of iron(II) piano-stool complexes proceeded *via* a relatively simple procedure (Scheme 1). This involved reduction of the dimer (compound **A**) with a dilute amalgam (sodium and mercury in THF) at room temperature to form the cyclopentadienyl dicarbonyl iron anion or cyclopentadienyl dicarbonyl metalate (Compound **B**). The nucleophilic anion was reacted *in situ* with the desired electrophile in which the various reactions proceeded *via* a nucleophilic substitution reaction. The reactions involved initial



Scheme 1. Synthesis of iron(II) piano-stool complexes used as catalysts for the synthesis of SCNMs.

attack of the nucleophilic anion (metalate) on the electron deficient carbon centre of the electrophile. The carbon centre of the electrophile was directly bonded to an electronegative halogen which serves as the driving force for the reaction to proceed.

SCNMs synthesized by using iron(II) piano-stool complexes as catalysts

Yield of SCNMs

The yields of SCNMs obtained from the nitrogen-containing catalysts (**1** and **2**) are summarized in Table 1. For both catalysts, the yield increased with increase in temperature from 800 to 900 °C. This could imply that the relatively lower temperatures were not conducive for the carbon precursor dissociation and dissolution into the iron catalyst or the iron particles were not of appropriate nanosize. Thus, increasing the reaction temperature favoured a faster supply of carbon and its dissolution into suitable catalyst nanoparticles and, subsequent precipitation, resulting in the formation of more SCNMs (Table 1). The results show an overall increase in yield with increase in temperature.

Also, in general, catalyst 2 (containing one oxygen and two nitrogen atoms) showed a higher yield than catalyst 1 (containing one nitrogen and two oxygen atoms). The higher yield observed with catalyst **2** is attributed to the relatively lower oxygen content. Oxygen is known to have a 'cleaning effect' since it can react with carbon (dangling carbon structures on the walls of SCNMs and amorphous carbon) to form CO_x which exit the reaction chamber as exhaust gases [26]. However, an excessive increase in oxygen abundance reduces the supply of carbon required to form SCNMs which results in lower yields. In the case of catalyst 1. at 850 °C, it showed a higher yield than catalyst 2. This is difficult to conclude on, but we can only stipulate that at this particular temperature catalyst 1 gives more products, mainly carbon spheres and amorphous carbon, but the conditions are not conducive enough for the formation of CNTs. A similar observation was made by Bepete et al. who reported a decrease in yield with increase in temperature in the presence of oxygen [30]. Hence, the reaction mechanism at different temperatures and the intermediate products formed need to be probed further.

The yields of SCNMs obtained from the sulfur-containing catalysts (**3**, **4** and **5**) are presented in Table 2. For these catalysts, the yield increased with increase in temperature in a similar manner as that observed for the nitrogen-containing catalysts. This further suggests that higher temperatures are more favourable for the synthesis of SCNMs when using heteroatom (nitrogen or sulfur) functionalized iron(II) piano-stool complexes as catalysts. At a synthesis temperature of 800 °C the yield increased with increase in the catalyst carbon content (i.e. **3** < **4** < **5**). At synthesis temperatures of 850 and 900 °C the yields tended to decrease with increase in ligand chain length at similar temperature conditions, except for catalyst **4** at 850 °C. This phenomenon was contrary to expectations; a possible explanation is that at higher temperatures

Table 2

Yield, distribution, size and thermal stability of SCNM products synthesized with catalysts **3**, **4** and **5** at 800, 850 and 900 °C.

Catalyst	T _{max} (°C)	Yield (mg)	SCNMs (distribution %)	Mean diameter (nm)	Decomposition temperature (°C)
3	800	35	CSs (89), AC (11)	827	592
	850	183	CSs (95), AC (5)	1003	635
	900	300	CSs (96), AC (4)	1433	611
4	800	72	CSs (93), AC (7)	875	648
	850	244	CSs (95), AC (5)	1242	671
	900	290	CSs (98), AC (2)	1574	685
5	800	210	CSs (94), AC (6)	988	431
	850	234	CSs (98) AC (2)	1239	458
	900	254	CSs (98) AC (2)	1448	465

CSs: Carbon Spheres; AC: Amorphous Carbons; T_{max} : Maximum set reaction temperature.

the sulfur could effectively react with carbon in the gas phase thus retarding the rate of carbon supply or with the iron nanoparticles leading to catalyst poisoning.

Effect of nitrogen and sulfur on the morphology of SCNMs

TEM and SEM analysis revealed that the nitrogen-containing catalysts 1 and 2 formed N-CNTs and CSs as the only SCNMs (Table 1). At a temperature of 800 °C catalyst 1 yielded CSs as the only SCNMs. An increase in temperature to 850 and then 900 °C led to the formation of both N-CNTs and CSs with the higher temperature favouring the formation of more N-CNTs and a decrease in formation of CSs. In the case of catalyst 2, a mixture of N-CNTs and CSs formed at all synthesis temperatures (Table 1). As the temperature was increased from 800 to 900 °C the abundance of N-CNTs increased while that of CSs decreased. This implied that for both catalysts 1 and 2 higher synthesis temperatures are favourable for N-CNT production while the relatively lower temperatures favour CS production. It is important to note that catalyst 2 yielded N-CNTs at all temperatures indicating that it is more effective in the synthesis of N-CNTs compared with catalyst 1. Catalyst 2 had a higher nitrogen content and lower oxygen content than catalyst 1. It is therefore plausible that the higher nitrogen content facilitated N-CNT growth while the higher oxygen content retarded N-CNT growth [31]. Similarly, Mohlala et al. [32] have observed that the presence of oxygen during synthesis can poison the catalyst thus reducing CNT formation.

TEM images of N-CNTs obtained by using catalysts **1** and **2** exhibited the presence of bamboo compartments (Fig. 1). Such bamboo compartments are associated with nitrogen-doping of CNTs [17]. The presence of nitrogen was also evidenced from qualitative analysis of the N-CNTs by use of energy dispersive X-ray spectroscopy (EDS) (Supplementary Material S1). In some instances the N-CNTs exhibited a coiled morphology (Supplementary Material S1) similar to that observed in a previous study in which nitrogen was used during synthesis [33]. The N-CNTs synthesized from catalyst **2** contained more bamboo compartments of shorter

Table 1

Yield, distribution, size and thermal stability of SCNM products synthesized with catalysts 1 and 2 at 800, 850 and 900 °C.

Catalyst	T_{max} (°C)	Yield (mg)	SCNMs (distribution %)	Bamboo compartment length (nm)	^a Mean diameter (nm)	Decomposition temperature ($^{\circ}C$)
1	800	63	CSs (80), AC (20)	_	_	
	850	182	T (25), CSs (70), AC (5)	65.4	44	509
	900	254	T (35), CSs (60), AC (5)	40.1	41	477
2	800	88	T (20), CSs (70), AC (10)	32.3	22	525
	850	165	T (40), CSs (50), AC (10)	30.1	23	517
	900	289	T (50), CSs (45), AC (5)	28.8	25	498

T: tubes; CSs: Carbon Spheres; AC: Amorphous Carbons; T_{max}: Maximum set reaction temperature.

^a Tube mean outer diameter (OD).



Fig. 1. TEM images of N-CNTs obtained at 900 °C from (a) catalyst 1 showing long bamboo compartments and (b) catalyst 2 showing short bamboo compartments.

lengths compared with those synthesized from catalyst **1** (Fig. 1 and Table 1). Since the bamboo compartments are brought about by nitrogen-doping, the higher quantities and reduced lengths of the bamboo compartments implied a higher N-content in N-CNTs from catalyst **2** [18]. This is attributed to the presence of more nitrogen atoms in catalyst **2** than in catalyst **1**, which resulted in increased nitrogen-doping levels of N-CNTs.

It is also important to note that the length of the bamboo compartments of N-CNTs synthesized from catalyst **1** and **2** decreased with increase in synthesis temperature (Table 1). This is an indication that as the temperature was increased the level of nitrogen-doping also increased which suggests that a higher temperature is a more favourable condition for N-CNT formation. Comparable observations were made by Keru et al., who also reported an increase in nitrogen-doping with increase in temperature [19]. Other reports, however, indicate that an increase in temperature results in a decrease in the amount of nitrogen incorporated into the CNTs [34]. The discrepancy between the results we obtained and those reported by other authors is attributed not only to the different methods used during synthesis but also the kind of catalyst and nitrogen source used.

The average outer diameters (OD) of N-CNTs obtained with catalysts 1 and 2 are summarized in Table 1. Representative OD distribution histograms are available in the Supplementary Material (S2). The mean ODs of N-CNTs obtained with catalyst 2 are smaller than those from catalyst 1. This can be due to more nitrogen-doping in N-CNTs obtained from catalyst 2 or smaller iron catalyst nanoparticles formed during synthesis [35-37]. It was also observed that T_{max} influenced the OD of the N-CNTs. The OD of the N-CNTs obtained from catalyst 2 increased with increase in temperature. The increase in OD with increasing temperature is in accordance with other reports [19]. A possible explanation is that as the temperature increases, collisions between iron catalyst particles increased resulting in more frequent collisions of iron nanoparticles (NPs) and more coalescence, which resulted in larger iron NPs and thus the production of larger ODs for the N-CNTs. However, very large particle sizes are known to be unsuitable for N-CNT formation, instead they are known to favour the formation of CSs, and if the size becomes too large, then AC is realized [26].

The sulfur containing catalysts **3**, **4** and **5** yielded CSs as the only SCNMs (Table 2 and Fig. 2). Thus, the presence of sulfur in the catalysts seemed to promote the formation of CSs and not CNTs or any other SCNMs. Other literature reported the effects of sulfur to be concentration dependant, with high concentrations of sulfur resulting in catalyst poisoning [26]. Although the amount of sulfur atoms introduced in the reactor *via* the catalyst is low, the interatomic distance of the heteroatom to the iron centre in organometallic complexes has been shown to lead to the same effects as

high concentrations of the heteroatom. It is possible that poisoning of the catalyst occurred and that spheres were formed without the aid of the metal catalyst. In a related study, Mohlala et al. have studied the effects of sulfur on the synthesis of SCNMs by using ferrocenyl sulfide or ferrocene mixed with either thiophene or S_8 [38]. Their findings show that the presence of large amounts of sulfur in the reactant mixture generated only amorphous carbon, while lower amounts of sulfur led to mixtures of MWCNTs and carbon fibres. Also, the product distribution, yield and tube diameters varied with the sulfur content.

The diameters of the CSs obtained with catalysts **3**, **4** and **5** were measured from the TEM images. For each reaction temperature, at least 100 CSs were measured and the mean diameters are presented in Table 2. Representative histograms of the diameter distribution of CSs are available in the Supplementary Material (S3). The average diameters of the CSs increased with an increase in the T_{max} for all the sulfur-containing catalysts. As the temperature increased, more carbon deposition may have occurred on the CSs which lead to an increase of the mean diameter.

As the ligand chain length increased, the mean diameters of CSs increased for samples obtained at a temperature of 800 °C (i.e. 827 < 875 < 988 nm). However, at 850 and 900 °C the mean diameters of CSs increased with increase of chain length from catalyst 3 to 4 then reduced with catalyst 5. This could imply that at 800 °C, as the ligand chain length increases, more carbon is present in the catalysts leading to more carbon deposition on the CSs, which results in an increase of the diameters. In the case of catalyst 5, there was a general increase of diameter (988 < 1239 < 1448 nm) with increase in temperature, but compared with catalyst 4, specifically at 850 and 900 °C, we would have expected larger ODs, i.e. 1242 vs. 1239 and 1574 vs. 1448 nm at the respective temperatures. We can only stipulate that the OD size indifference, which in this case is not very significant, could have been as a result of other factors such as the difference in geometry (phenyl vs. alkane structure) and other physical properties of the three catalysts.

The TEM and SEM images of the CSs showed the presence of fused carbon spheres (Fig. 2). It is not unusual for spheres to aggregate and form necklace-like structures held together by van der Waals forces when they have diameters of 1000 nm or less [1]. These are normally formed during the synthesis and are not a result of post-synthetic treatments [1].

Crystallinity of SCNMs

The crystallinity of the SCNMs synthesized with catalysts **1** to **5** was determined by means of Raman spectroscopy. Two prominent peaks were observed at 1553 and 1350 cm⁻¹. The peak at 1553 cm⁻¹ represents the graphitic band (G-band) associated with graphitic carbons [39], while the peak at 1350 cm⁻¹ represents the disorder

Fig. 2. (a) TEM image and (b) SEM image of CSs synthesized by using catalyst 5 at 850 °C.

band (D-band) associated with vibrations between carbon atoms of disordered graphene sheets [40]. The ratio of the integrated areas of the D- and G-bands (I_D/I_G) was used to provide an indication of the crystallinity of the SCNMs. A relatively high I_D/I_G ratio is indicative of a less crystalline material, whilst a lower ratio indicates a more crystalline material. Fig. 3 displays the I_D/I_G ratios for SCNMs obtained from all catalysts at different temperatures.

For the nitrogen-containing catalysts 1 and 2, the I_D/I_G ratios generally increased with rise in synthesis temperature. This indicated that the N-CNTs became less crystalline as the temperature was increased. A decrease in crystallinity can be caused by increased nitrogen-doping levels in N-CNTs or an increase in the amount of AC [19]. Since the amount of AC did not increase with increase in temperature (Table 1), the decreased crystallinity was mainly attributed to the increase of nitrogen content in the N-CNTs with increasing temperatures. This observation further supports the increase in nitrogen-doping with increase in temperature observed from TEM analysis (see Effect of nitrogen and sulfur on the morphology of SCNMs section). Additionally, a higher I_D/I_C ratio was observed for the samples obtained from catalyst 2 compared with those of catalyst 1. This was attributed to higher incorporation of the nitrogen atoms into the structures of the N-CNTs (nitrogen-doping) obtained with catalyst 2 compared with those produced from catalyst 1. This is also consistent with data presented in Effect of nitrogen and sulfur on the morphology of SCNMs section under the discussion on the bamboo compartments, sizes and implications.

Fig. 3. I_D/I_G ratios of SCNMs synthesized with catalysts 1 to 5 at 800, 850 and 900 °C.

For the sulfur-containing catalysts, a reaction temperature of 800 °C generally yielded the most disordered CSs as they had a higher I_D/I_G ratio compared with CSs obtained at 850 and 900 °C. Crystallinity was observed to increase as the temperature was increased (decreasing I_D/I_G). This is in agreement with literature, where higher temperatures have been shown to be conducive for the formation of more graphitic CSs [1]. Under similar T_{max} , the crystallinity of the CSs was observed to increase with increase in ligand chain length, with catalyst **5** producing the most crystalline CSs.

Dependence of thermostability of SCNMs on nitrogen and sulfur

Thermogravimetric analysis (TGA) measurements were conducted to obtain information on the thermal stability of the SCNMs obtained from the various catalysts. The TGA runs were conducted in triplicates to verify reproducibility. The TGA decomposition temperatures of the synthesized materials are listed in Tables 1 and 2 The TGA curves of SCNMs obtained from all catalysts are provided in the Supplementary Material (S4). For the SCNMs synthesized with catalysts 1 and 2, there was a decrease in thermal stability as the temperatures increased. This correlated with the increased level of nitrogen-doping in the N-CNTs as the temperature was increased (see Effect of nitrogen and sulfur on the morphology of SCNMs section). The increase in nitrogen-doping levels increased the density of structural defects in N-CNTs thus reducing their thermal stability [30].

In the case of the sulfur-containing catalysts, it was generally observed that the decomposition temperatures increased as the T_{max} was increased. This trend implied that higher temperatures enhanced the production of more graphitic spheres. This observation also supports the observed decreasing trend in the I_D/I_G ratios as the temperature increased. However, catalyst 3 did not follow this trend, with a temperature of 850 °C, producing the most thermally stable spheres for this catalyst. A possible explanation could be that the CSs obtained with catalyst 3 at a reaction temperature of 850 °C had a narrower diameter distribution compared with the other two reaction temperatures for this catalyst. A narrow diameter distribution of spheres can exhibit narrow decomposition temperature ranges. The CSs obtained at 800 and 900 °C could possibly have a wider diameter distribution leading to a combination of low and high decomposition temperatures within the same sample thus resulting in an overall lowering of the decomposition temperature of the whole sample.

The most thermally stable CSs were obtained with catalyst **4**. As the ligand chain length increased from catalyst **3** to **4**, thermal stability of CSs synthesized under similar T_{max} conditions was observed to also increase. A further increase in the ligand chain length (catalyst **5**) resulted in a decrease of the thermal stability of the CSs. This trend cannot be easily and conclusively explained

especially when, in general, products from catalyst **5** were deemed to be more crystalline by Raman analysis (see Crystallinity of SCNMs section) and the only differences, which were also not very consistent, were on the effect of diameter size and the distribution of the SCNMs on the thermal stability. Hence, this needs further probing.

Conclusions

Nitrogen- and sulfur-containing iron(II) piano-stool complexes were successfully synthesized and used as novel catalysts for the synthesis of N-CNTs and CSs. Nitrogen-containing iron(II) piano-stool complexes were selective towards N-CNT formation while, sulfur-containing complexes were selective towards formation of CSs. Nitrogen and sulfur heteroatoms were also used to modulate size, crystallinity and thermostability of the formed SCNMs. Increasing the nitrogen content in the catalyst, increased the level of nitrogen-doping in N-CNTs, which in turn had an effect on the physical properties of the N-CNTs. Overall, catalyst **2** was better than catalyst **1** for the synthesis of higher nitrogen-containing N-CNTs. Varying the chain length of the sulfur containing compounds altered the physical properties of the formed CSs.

A study on synthesis temperature proved to be a useful approach to tuning the physical properties of the synthesized SCNMs. For example, in the case of nitrogen-containing catalysts, higher temperatures favoured higher nitrogen-doping levels in the N-CNTs, which in turn influenced the crystallinity and thermostability of these samples. While in the case of the sulfur-containing catalysts, the crystallinity of CSs increased with increase in temperature for catalysts **3** and **5** and also, in general, larger diameters were realized. Thus, synthesis conditions, the heteroatoms present in organometallic catalysts, and the catalyst ligand chain length, play vital roles in controlling the obtained SCNMs, which in turn can be used to tune the physical properties of the products obtained.

Experimental

Instrumentation

A Bruker 400 MHz Advance or 600 MHz Ultrashield NMR spectrometer was used to obtain the ¹H and ¹³C NMR spectra at room temperature in CDCl₃ as the solvent. Melting points were recorded on a Stuart Scientific, model SMP3, melting point apparatus. For each sample three reproducible melting point readings were taken and averaged. Elemental analyses were performed on a LECO CHNS-932 elemental analyser which was standardized with acetanilide. Products of the SCNM synthesis were characterized by transmission electron microscopy (TEM) (JEOL JEM 1010), scanning electron microscopy (SEM), (JEOL 2100), thermogravimetric analysis (TGA) (TA Instruments Q SeriesTM thermal analyzer DSC/TGA (Q600)) and Raman spectroscopy (Delta Nu Advantage 532TM).

Chemical reagents, solvents and gases

All reagents were synthetically pure and used as supplied unless otherwise stated. Iron pentacarbonyl (97%), 2-chloroethyl methyl sulfide (97%), 2-chloroethyl ethyl sulfide (98%), 2-chloroethyl phenyl sulfide (98%), 2-chloro-*N*,*N*-dimethylpropylamine hydro-chloride (98%), *N*-(bromomethyl)phthalimide (97%) and 2-(4-chlorophenyl)ethylamine (98%) were products of Sigma–Aldrich Chemical Co. (St. Louis, USA). Sodium (99.5%) and mercury (99.5%) were supplied by Riedël de Haën (Seelze, Germany) and Rochelle Chemicals (Johannesburg, South Africa), respectively. The 3-bromomethyl-2(*1H*)-quinoxalinone (90%) was supplied by Alfa Aesar (Karlsruhe, Germany).

All solvents were dried and freshly distilled before use. Reactions were carried out under ultra-high-purity N₂ or Ar atmospheres (Afrox, South Africa). Analytical and reagent grade solvents were used for reactions. Dicyclopentadiene (diCp) (97%), pentane, tetra-hydrofuran (THF), toluene, dichloromethane (DCM) and diethyl ether were products of Merck (Schuchardt, Germany). Deuterated chloroform (CDCl₃) was supplied by Sigma–Aldrich Chemical Co. (St. Louis, USA). Argon gas of ultra-high-purity (99.999–100%, $O_2 \leq 3$ ppm, moisture ≤ 2 ppm) was purchased from Afrox Limited Gas Co. (Durban, South Africa). Silica gel (0.040–0.063 mm), neutral aluminium oxide 90 (0.063–0.200 mm), and thin-layer chromatography plates were all supplied by Merck (Schuchardt, Germany).

Synthesis and characterization of iron(II) piano-stool complexes

General procedure

Synthesis of dicyclopentadienyl iron carbonyl dimer (compound **A**, Scheme 1) was carried out as previously reported [41]. In brief, dicyclopentadiene and iron pentacarbonyl were reacted under an atmosphere of argon for 8 h at 150 °C. After cooling and filtering, the crude product was recrystallized by using a mixture of pentane and dichloromethane (3:1 v/v) to obtain compound **A**.

The procedure for the synthesis of the compounds 1, 2, 3, 4 and 5 (Scheme 1) was similar, and related to a previously reported procedure [42]. Briefly, an amalgam was formed by reacting mercury with sodium. Compound A was added to the amalgam to form the nucleophile/salt, compound **B**. Compound **B** was subsequently introduced into a beaker and reacted with one of the following electrophiles: *N*-(bromomethyl)phthalimide. 3-bromomethyl-2(1H)-quinoxalinone, 2-chloroethyl methyl sulphide, 2-chloroethyl ethyl sulphide or 2-chloroethyl phenyl sulphide to form compounds 1, 2, 3, 4 or 5 respectively. The experimental procedures for the synthesis and characterization of compounds 1 to 5 are detailed in the Supplementary Material (S5). Herein, a brief description of the experimental procedures for the synthesis and characterization of two new compounds (1 and 2) are detailed. All the compounds were characterized by means of standard methods including melting point determination, ¹H NMR, ¹³C NMR, IR studies and mass spectrometry as detailed below.

Synthesis of dicarbonyl(η^5 -cyclopentadienyl) (N-phthaloylaminomethyl)iron(II) (**1**)

The general procedure outlined in General procedure section was followed to obtain compound **1** as a yellow powder. Yield: (1.074 g, 80%): m.p. 181 °C, ¹H NMR (400 MHz, CDCl₃, ppm) $\delta_{\rm H}$ = 4.05 (2H, s, Fe–CH₂), 4.91 (5H, s, C₅H₅), 7.70 (4H, m, C₆H₄). ¹³C NMR (100 MHz, CDCl₃, ppm) $\delta_{\rm C}$ = 11.14 (Fe–CH₂), 85.36 (Cp moiety), 122.5 (2C, Ar-CH), 132.8 (2C, Ar–C), 133.4 (2C, Ar–CH), 168.7 (NCO), 215.5 (terminal CO). IR (ATR, cm⁻¹) 1997 (terminal CO), 1951 (terminal CO), 1751, 1701. CHN analysis for C₁₆H₁₁FeNO₄ Calculated: C; 57.01, H; 3.29, N; 4.15. Found: C; 57.16, H; 3.34, N; 4.18.

Synthesis of dicarbonyl(η^5 -cyclopentadienyl) (quinoxalin-2(1H)onemethyl)iron(II) (**2**)

The general procedure outlined in General procedure section was followed to obtain compound **2** as a yellow powder. Yield: (0.952 g, 69%): m.p. 149 °C. ¹H NMR (600 MHz, CDCl₃, ppm) $\delta_{\rm H} = 2.66$ (2H, s, Fe–CH₂), 4.87 (5H, s, C₅H₅), 5.81 (1H, s, NH), 7.35 (2H, dd, m, C₆H₂), 7.51 (1H, d, ³*J*_{HH} 8.0, C₆H), 7.83 (1H, d, ³*J*_{HH} 8.0, C₆H). ¹³C NMR (150 MHz, CDCl₃, ppm) $\delta_{\rm C} = 10.03$ (Fe–CH₂), 85.04 (Cp moiety), 114.4 (Ar-CH), 124.1 (Ar-CH), 125.5 (Ar-CH), 130.9 (Ar-CH), 133.5 (Ar–C), 156.3 (Ar–C), 163.8 (NCO), 217.4 (terminal CO). IR (ATR, cm⁻¹): 3406 (N–H stretch), 1998 (terminal CO), 1942 (terminal CO), 1658. CHN analysis for C₁₆H₁₂FeN₂O₃ Calculated: C; 57.17, H; 3.60, N; 8.33. Found: C; 57.49, H; 3.65, N; 8.41.

Synthesis and characterisation of SCNMs

A CVD floating catalyst method was used for the synthesis of the CNTs, N-CNTs and other SCNMs by using compounds 1, 2, 3, 4 and 5 as catalysts. The setup of the reactor used was based on similar designs reported in the literature [27]. Briefly, a quartz tube $(850 \times 27 \text{ mm i.d.})$, used as the reactor vessel, was placed inside a muffle/tube furnace (model no. TSH12/50/610. Elite Thermal Svstems Ltd) fitted with a main zone furnace controller (Eurotherm 2416). At one end of the guartz reactor tube a guartz water-cooled injection port was fitted, and at the other end a glass cold finger was fitted. The carrier gas and reducing agent, 10% hydrogen in argon (v/v), was supplied to the system at a rate of 100 mL min⁻¹ at 80 kPa. The furnace was set to heat at 10 °C min⁻¹ to reach the desired maximum temperature ($T_{max} = 800, 850$ and $900 \circ C$) for the various reactions. The system was purged for 10 min with the carrier gas, a mixture of hydrogen/argon gas (10:90H₂:Ar (v/v)), before each reaction. A solution of 2.5 wt.% catalyst/toluene was prepared for all the reactions carried out, by weighing out 0.275 g of catalyst in 11 mL toluene. Once the set T_{max} was reached and purging completed, 7.5 mL of catalyst solution was injected with a syringe (SS 150 mm L non-boring 24 gauge bevelled-tip needle) into the quartz reactor. The furnace was maintained at the set T_{max} for 30 min; afterwards the reactor was allowed to cool to room temperature.

Only carbonaceous material deposited in the hot zone of the reactor was collected for analysis. The SCNMs produced by these iron(II) piano-stool catalysts were characterized by TEM and SEM to determine their type, distribution and morphology. Energy dispersive X-ray spectroscopy (EDS) was used to provide qualitative evidence of heteroatom-doping, in this case nitrogen-doping and is not presented herein. The distribution and average size of the SCNMs was determined by counting procedures and the results represent average values obtained from electron micrographs. The nanotube yield was calculated from the wt.% of the products obtained relative to the mass of the solution injected into the system. Raman spectroscopy and TGA were used to characterize the crystallinity and thermal stability, respectively. The effects of reaction temperature (T_{max}) on the SCNMs distribution and yield were also investigated.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jorganchem.2014.12.038.

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