

Functionalization of Carbon Nanotubes with a Metal-Containing Molecular Complex

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ABSTRACT

Raw and oxidized carbon nanotubes have been reacted with Vaska's complex. It has been found that Ir coordinates to these nanotubes by two distinctive pathways. With raw nanotubes, the process is through a η^2 -coordination process. With oxidized nanotubes, the reaction occurs by coordination through the increased number of oxygen atoms, forming a hexacoordinate structure around the Ir atom. The reaction process significantly increases oxidized nanotube solubility in dimethylformamide.

Single-walled carbon nanotubes (SWNTs)¹ have been the focus of intensive study due to their unique structure-dependent electronic and mechanical properties.^{2–5} Understanding the chemistry of single-walled carbon nanotubes (SWNTs) is critical to rational manipulation of their properties. The ability to disperse and solubilize carbon nanotubes would also open up new prospects in aligning and forming molecular devices. Nonetheless, this objective necessitates controlled chemical functionalization of tubes, a relatively unexplored area of research. Indeed, SWNTs have been fluorinated⁶ by means of reaction with elemental fluorine; derivatized in organic solutions with thionylchloride and octadecylamine,⁷ as well as with chlorine through the use of dichlorocarbene; ultrasonicated⁸ in a monochlorobenzene solution of poly(methyl methacrylate); and noncovalently functionalized⁹ using a bifunctional molecule, 1-pyrenebutanoic acid, succinimidyl ester to form amide bonds for protein immobilization. Chemical functionalization of SWNTs attached to conventional atomic force microscopy probes has also been demonstrated as a methodology of yielding high-resolution, chemically sensitive images on samples containing multiple chemical domains.¹⁰

However, there has not been as much effort in treating nanotubes as chemical reagents (be it inorganic or organic) in their own right, which would expand the breadth of reactivity these tubes can undergo. In this Letter, we report the synthesis of nanotubes covalently complexed to molecular coordination compounds. Specifically, both oxidized nano-

tubes and raw, unfunctionalized nanotubes have been reacted with Vaska's compound, *trans*-IrCl(CO)(PPh₃)₂, to form covalent nanotube–metal complexes. This functionalization process not only opens up the area of metallo-organic chemistry to nanotubes but also suggests potential applications in catalysis and molecular electronics. Moreover, the complexes of oxidized nanotubes with Vaska's compound are much more soluble in dimethylformamide (DMF) than raw tubes, a finding that should facilitate the chemical manipulation as well as the photophysical analyses of these materials.

Conceptually, the novelty of this derivatization is that the nanotube can be considered as a primary ligand, as a functional moiety like any other, with respect to the central metal atom, Ir. In effect, iridium was found to coordinate to our nanotubes in several distinctive bonding arrangements, depending on the oxidation state of the nanotube. Results were confirmed by ³¹P NMR spectroscopy (Bruker AC-250 multinuclear FT-NMR), FT-IR spectroscopy (Mattson Galaxy FT-IR 3000 spectrophotometer), electron ionization mass spectroscopy (a Varian Saturn 2000 with a capability of measuring up to *m/z* 650 and a Fennigan model with a capability of measuring up to *m/z* 4000), as well as data from transmission electron microscopy (TEM) (Philips CM-12 scope) and energy-dispersive X-ray analysis (EDX).

Raw SWNTs bundles (Carbox: length range of 0.8–1.2 μ m; \sim 35–50 nm in width) were initially oxidized according to existing procedures¹¹ involving KMnO₄. To summarize, 1 g of nanotubes was sonicated and then refluxed for 5 h in a boiling solution of approximately 1.5 M KMnO₄ in sulfuric acid. Upon filtration, the tubes were washed

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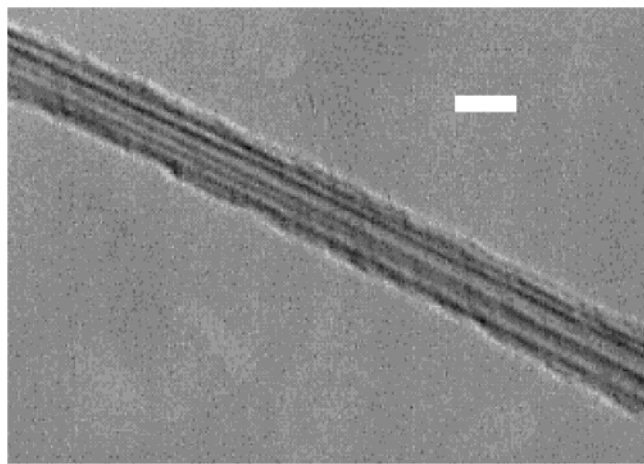


Figure 1. Transmission electron micrograph of purified and oxidized single-walled carbon nanotubes (SWNTs). The scale bar on the figure represents 10 nm. Samples examined by transmission electron microscopy (TEM) were dispersed in ethanol, sonicated for 1 min, and then evaporated onto a 300 mesh copper grid coated with carbon lacey film. A Philips CM12 instrument was used to analyze these materials at an accelerating voltage of 120 kV. Functionalization with Vaska's complex does not alter the intrinsic structural integrity of the tube.

extensively with 12.1 N HCl to dissolve away all of the MnO_2 and further washed multiple times with distilled, deionized water. This method¹² is expected to coat the nanotube sidewalls with keto, carboxylic, aldehyde, and alcoholic groups. It is also expected that analogous chemistry will occur with nanotube bundles as well, opening the way for similar types of functionalization as with single SWNTs. TEM analyses showed that the oxidation process not only removed most of the amorphous carbon but also the majority of metal particles (Figure 1). The purified tubes were then dried in a vacuum oven at 180 °C. The air-sensitive reaction with Vaska's compound was then carried out on a standard Schlenk apparatus under a dinitrogen atmosphere. Oxidized as well as unpurified nanotubes were sonicated for 2 min in anhydrous DMF, prior to mixing with varying quantities $[(0.6\text{--}1.2) \times 10^{-3} \text{ M}]$ of *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (Aldrich), dissolved in freshly distilled DMF. The mixtures were stirred vigorously for 12 h under nitrogen at 50 °C. It was found that the oxidized nanotubes quickly dissolved into solution, yielding a dark brownish-yellow, clear liquid, that is rather stable. In fact, the tubes did not precipitate out even after 3 months. The solubility of the tubes varied with the concentration of Vaska's complex added, suggesting that dissolution was in fact chemically induced. The solubility of a typical sample in DMF at room temperature was $\sim 250 \text{ mg/L}$, about 1 order of magnitude improvement over that found for unmodified tubes.¹³ Our results with oxidized nanotubes, but otherwise unmodified with Vaska's complex or any other moiety, showed a solubility of $\sim 25\text{--}35 \text{ mg/L}$.

Upon excess solvent removal, the reaction mixture was allowed to cool at 5 °C for 72 h; though no single crystal formation was observed in this process, this step was important for the coordination process to occur. A dark brown powder was obtained on removing solvent from the oxidized nanotube/Vaska's complex (ONTV) mixture; no-

tably, it could readily be redissolved in DMF, demonstrating the reversibility of the dissolution process. It has been found that the ONTV product itself is relatively stable toward air and moisture; in fact, characterization of the sample was carried out under ambient conditions with no trace of degradation observed after 3 months.

The unoxidized carbon nanotube/Vaska's complex (UNTV) mixture was filtered through a $0.20 \mu\text{m}$ Nylon 6,6 membrane and washed thoroughly with DMF and ethanol. The UNTV sample is barely soluble in DMF, even at elevated temperatures, with an estimated solubility of less than 10 mg/L .

Mass spectrometry data on our synthesized structures indicated that bonding of Vaska's complex to the tubes is likely to be associative; that is, Vaska's complex does not break apart during this complexation process. Indeed, for the ONTV compound in DMF, the strong m/z peak at 227 corresponds to an Ir-Cl fragment, indicating conservation of this bond structure in the adduct. A m/z peak at 415 can be correlated with an $\text{IrCl}(\text{PPh}_2)$ moiety, whereas other peaks can be assigned to PPh, PPh_2 , $\text{Ir}(\text{CO})\text{Cl}$, and PPh_3 groups, respectively. Likewise, data from the UNTV aggregate illustrate the presence of PPh, PPh_2 , and PPh_3 groups as well as Ir-(CO) and Ir-Cl bonds in that molecular metal nanotube complex.

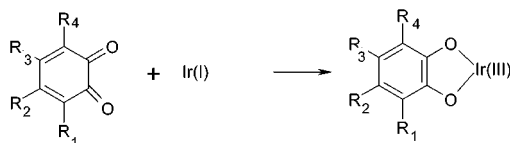
Further TEM results showed that the derivatization process did not appear to damage the tubular structure. In fact, the oxidized SWNT rope/bundle widths were approximately 20–25 nm, whereas the metal complexed tubes had a dimensional range of 25–40 nm, which is consistent with the expectation of an extensive heavy metal coating on the tubes themselves. Moreover, EDX analyses on the molecular metal complexes were in agreement with a spatial localization of Ir, Cl, and P elemental signatures on the functionalized tubes.

Vaska's compound is particular in that the magnitude of the stretching frequency for the coordinated carbonyl group is extremely sensitive to changes in the environment of the central metal atom.¹⁴ The infrared spectrum (KBr pellet) showed the presence of a carbonyl stretching peak at 1954 cm^{-1} for a pure, unreacted powder of Vaska's complex. For the ONTV complex, this peak shifts to 2068 cm^{-1} and for the UNTV complex, it appears at 2002 cm^{-1} . The shift to a higher frequency would be expected from a contribution of two factors, namely reduced back-donation from the metal to the π^* antibonding orbital of the CO molecule when an electron withdrawing ligand, such as an electron deficient alkene, coordinates to a transition metal atom and, second, a synergistic decrease in σ -bond donation from the CO to the central metal atom.

Published work¹⁵ on reactions of pure Vaska's complex with electron-deficient olefins, such as tetracyanoethylene (TCNE) and tetrafluoroethylene (TFE), has demonstrated that the carbonyl stretching frequency in these adducts can be used to measure the degree of electron withdrawal from the metal in the adducts. For the TFE case, the CO stretching frequency has a value of 2052 cm^{-1} , whereas for the TCNE example, the corresponding value is 2057 cm^{-1} . A fullerene adduct¹⁶ had a CO stretching frequency at 2014 cm^{-1} . Thus, our data indicate that the modes of coordination of iridium

to the nanotube are different depending on whether the tubes were oxidized or not. There is also a distinct possibility that Vaska's compound may have reacted with fullerene-like species present as impurities in our samples, for instance, to the poles of C_{70} . However, ^{31}P NMR studies of DMF washings of the UNTV sample show predominantly unreacted Vaska's complex and, significantly, a very low concentration of fullerene adducts (which are somewhat soluble in DMF). In combination with FT-IR data (in the Supporting Information), which show a sharp, strong carbonyl signal at a position for the nanotube adducts, distinct from that of the fullerene adducts, this collection of evidence suggests that while fullerene adducts in our UNTV sample are undoubtedly present, it is likely that Vaska's complex bonds predominantly to the nanotubes themselves.

In effect, it is theorized that the unoxidized tubes likely coordinate as an electron deficient alkene in a η^2 manner. Whereas for the oxidized tubes, the previous mechanism is a possibility, it is reasonable to expect that the coordination can more likely occur through the oxygen atoms coating the nanotube exterior. That is, oxidative addition is the more plausible option, considering that the outer surface of the tubes is oxygenated and that the Ir complex is extremely susceptible to this type of addition. One potential mechanism would involve carbonyl groups ortho to each other on a benzenoid ring, which could then add to the metal to generate a complex with an ortho-diolato ligand.¹⁷



It turns out that the carbonyl stretch for $\text{Ir}(1,2\text{-O}_2\text{C}_6\text{Cl}_4)\text{-(CO)Cl(PPh}_3)_2$, a six-coordinate complex containing Ir metal–oxygen bonds, is 2066 cm^{-1} , exceedingly close to the value found here for the ONTV complex, namely 2068 cm^{-1} . Further evidence for this conclusion comes from the presence of a sharp peak at 1193 cm^{-1} , due to a singly bonded C–O stretching vibration; in a pure sample of Vaska's complex, the corresponding value is 1100 cm^{-1} . The observed shift of about 100 cm^{-1} is characteristic of oxidative addition reactions, accompanied by reduced σ electron donation from the metal to CO in the resulting adduct. In addition, smaller peaks noted at 2244 and 868 cm^{-1} in the oxidized tube/complex results, but not in the UNTV complex spectra, can be attributed to $\nu(\text{Ir-H})$ and $\delta(\text{Ir-H})$ vibrations, respectively, which have been observed in a number of six-coordinate hydrido-iridium complexes.^{14,18} That particular structure can arise due to cleavage of heteronuclear O–H bonds in alcoholic and carboxylic groups followed by coordination of the resulting anionic fragments to the Ir metal atom.

Interpretation of UV–visible spectra of the ONTV adduct (in DMF with solvent correction) also supports the contention that the oxidized nanotubes likely undergo oxidative addition to Vaska's complex. In effect, the electronic spectrum of

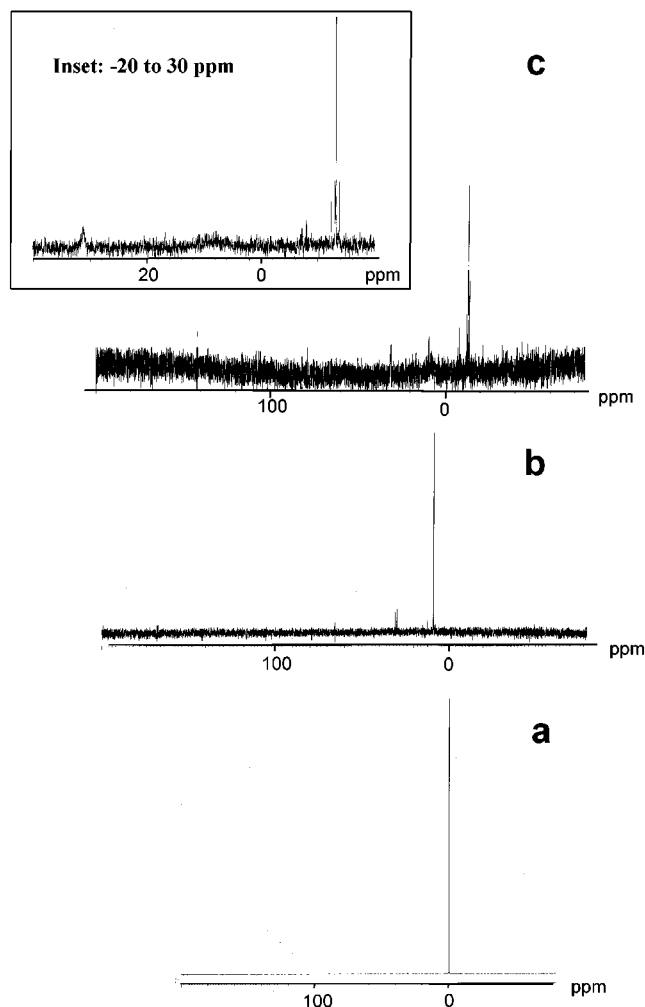


Figure 2. ^{31}P NMR spectra of (a) triphenylphosphine, (b) Vaska's compound, $\text{Ir(CO)Cl(PPh}_3)_2$, and (c) ONTV (oxidized carbon nanotube–Vaska's complex) aggregate, respectively. The spectra were taken at 250 MHz in d_7 -DMF on a Bruker AC250 at room temperature. The horizontal axis represents shift values in parts per million (ppm); the vertical axis represents signal intensity in arbitrary units. The chemical shift of triphenylphosphine is at -0.227 ppm ; for Vaska's compound, the P atoms are relatively deshielded and appear at 8.711 ppm . In the ONTV nanotube/metal complex adduct, the peaks are significantly shielded. The major peaks are located at -7.993 ppm as well as a cluster of four peaks located at -12.32 , -12.97 , -13.12 , and -13.77 ppm , respectively. The large number of peaks may arise from the presence of several modes of coordination as well as to the possibility of stereochemical inequivalence among the new adducts.

Vaska's complex contains distinctive absorption peaks at 340, 389, and 439 nm, due to metal–ligand charge transfer (MLCT) processes.¹⁹ The magnitude of the absorbance at 389 nm, in particular, has been commonly used to monitor the progression of oxidative addition reactions involving Ir(I) complexes.^{19–21} In fact, the disappearance of this intense peak is considered as a diagnostic¹⁹ for the conversion of Ir(I) to Ir(III). That is exactly what we have found with our ONTV complexes. The spectrum of oxidized nanotubes is featureless in this region.

Results from ^{31}P NMR (Figure 2) for the ONTV adduct in d_7 -DMF (Aldrich) further confirm the coordination of

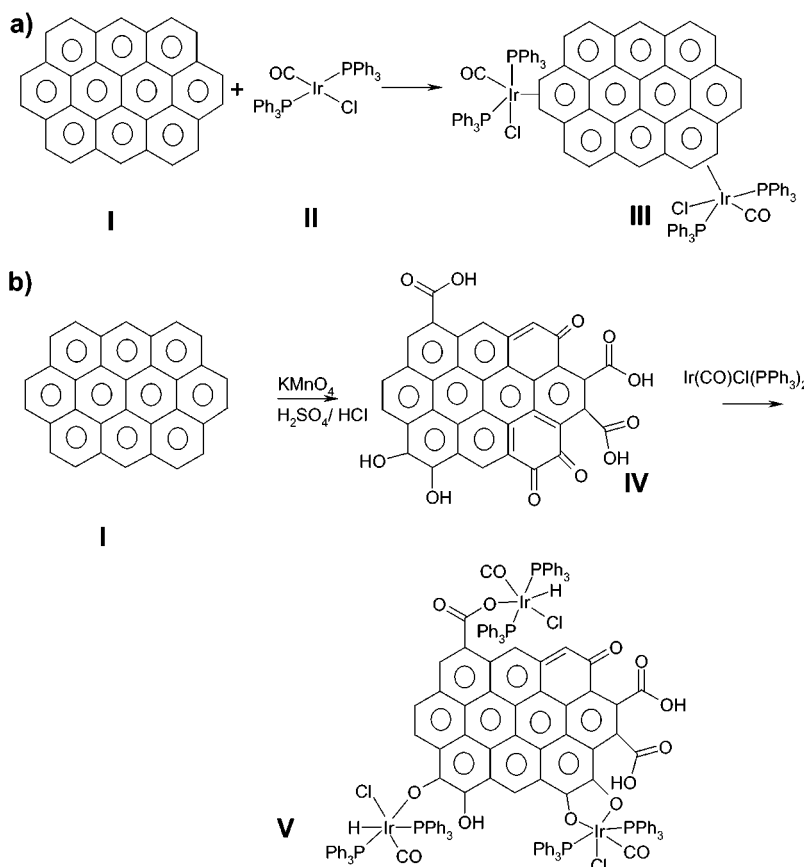


Figure 3. Proposed reaction scheme for the functionalization reactions of carbon nanotubes with *trans*-chlorocarbonylbis(triphenylphosphine)-iridium(I) (II). (A) Initial complexation of II with raw single walled nanotubes (I) produced a theorized η^2 -coordination complex, UNTV, (III). (B) Raw single walled carbon nanotubes were cleaned and purified by means of permanganate oxidation to yield oxidized carbon nanotubes (IV); addition of Vaska's complex (II) to the nanotubes yielded a nanotube-Vaska's compound adduct, ONTV (V); several possible modes of metal-nanotube coordination are illustrated.

Vaska's complex to the oxidized carbon nanotube.²² The resonances are sharp and the phosphorus atoms are shielded in the adduct. The data are consistent with a structure where the Ir metal center is coordinated to the oxygen atoms on the ONTV. In this scheme, the lone pair of electrons on the phosphorus atom is more localized on that atom due to the decrease of σ bond donation to the central Ir.

All the spectra collected were referenced to an identical, external phosphoric acid standard. The ^{31}P NMR of the ONTV complex is expanded as an inset in Figure 2c. The presence of a multitude of peaks suggests the potential of several modes of coordination. It is possible that the large relatively shielded peak at -12.97 ppm may correspond to influence on the coordination from carboxylate groups as those are the most abundant on the nanotube.¹² Significantly, this spectrum does not show any signals from dissociated triphenylphosphine, indicating that ligand binding is associative for the complexes. It thus follows that the association is not very different from the formation of a C_{60} adduct with Ir that has been previously described.²³

To summarize, a metal complex, more specifically, the coordinatively unsaturated Vaska's compound, *trans*-chlorocarbonylbis(triphenylphosphine) iridium(I), has been complexed with raw single walled nanotubes as well as with oxidized, purified nanotubes. The modes of coordination are different in each case.

The compound complexes to raw nanotubes by η^2 coordination across the graphene double bonds, as denoted in Figure 3a. In effect, ligand binding is an associative process with the formation of a π complex and is expected to be similar to that observed^{24,25} in $(\text{TCNE})\text{IrBr}(\text{CO})(\text{PPh}_3)_2$ or in the fullerene adduct.¹⁶ This type of reaction, in which the ligand acts as a weak base toward the metal complex, has also been referred to as a "reductive addition" (with respect to the metal).¹⁵ For the oxidized carbon nanotubes, coordination through the oxygen atoms seems a more likely possibility, in other words through an oxidative addition to form a hexacoordinate structure, as illustrated in Figure 3b. Oxidative additions to form $18e^-$ "coordinatively saturated" compounds are well-known for Vaska's compound and other related d^8 complexes and have been extensively studied.^{26,27} In fact, it is postulated that the oxidized nanotubes coordinate to the compound via oxidative addition to form an iridium-(III) complex.

Functionalization of oxidized nanotubes with Vaska's complex renders them soluble and stable in organic solution, thereby enabling further exploitation of their wet chemistry. Moreover, as the tubes are easily recoverable from solution, this finding has significant scientific and economic implications for nanotubes as reusable catalyst supports, particularly for expensive catalyst materials. Moreover, whereas the poor solubility of nanotubes has limited their role in homogeneous

catalysis, we are currently investigating the catalytic properties and reactivity of our synthesized complexes in the hydrogenation of alkenes. We expect similar types of nanotube coordination chemistry to be seen with other molecular complexes. Indeed, molecular metal complexation with nanotubes could provide the basis not only for various site-selective nanochemistry applications but also for the possibility of self-assembly of nanotubes with tailorable electronic properties, important for advances in molecular electronics.

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Supporting Information Available: Transmission infrared spectra (KBr pellet) of (a) Vaska's compound, (b) ONTV complex, and (c) UNTV complex, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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