Review Article
Theoretical Studies of Substitutionally Doped Single-Walled Nanotubes

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Received 1 September 2010; Accepted 19 November 2010

Academic Editor: Valery Khabashesku

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The rich chemistry of single-walled carbon nanotubes (SWCNTs) is enhanced by substitutional doping, a process in which a single atom of the nanotube sidewall is replaced by a heteroatom. These so-called heteroatom-substituted SWCNTs (HSWCNTs) exhibit unique chemical and physical properties not observed in their corresponding undoped congeners. Herein, we present theoretical studies of both main group element and transition metal-doped HSWCNTs. Within density functional theory (DFT), we discuss mechanistic details of their proposed synthesis from vacancy-defected SWCNTs and describe their geometric and electronic properties. Additionally, we propose applications for these nanomaterials in nanosensing, nanoelectronics, and nanocatalysis.

1. Introduction

Iijima’s pioneering work on carbon nanotubes (CNTs) [1] and single-walled carbon nanotubes (SWCNTs) [2] in the early 1990s sparked a general interest in both fundamental and practical nanotechnology. Over the past 20 years, research efforts have aimed to improve both efficiency and selectivity of nanotube synthesis, as well as understand their chemical reactivity and extraordinary electronic and thermal properties [3–5]. Carbon nanotubes have significant potential for application in molecular electronics [6–15], nanomechanics [16–20], optics [21–24], sensors [6, 25–31], and even catalysis [32].

The molecular structure of SWCNTs can be obtained by rolling up an infinite graphene sheet into a cylinder [33–40]. As illustrated in Figure 1, SWCNTs are characterized by a chiral (or circumferential) vector $\mathbf{AB}$, which is a linear combination of two unit lattice vectors $a$ and $b$. In other words,

$$\mathbf{AB} = ma + nb, \quad (1)$$

where $m$ and $n$ are integers. The pair of indices $(m,n)$ determines the diameter and chirality of the tube, as well as the basic electronic character. If $n = m$, the nanotube is classified as armchair and is metallic in nature (i.e., having a band gap of 0 eV). If $n \neq m$ and both $n$ and $m$ are nonzero, the nanotube is chiral. If $n - m = 3p$, where $p$ is a nonzero integer, the nanotube is semimetallic with a band gap on the order of meV [34, 37]. If $n - m \neq 3p$, where $p$ is a nonzero integer, the nanotube is semiconducting with a band gap on the order of 1 eV. Figure 1 also highlights the wrapping direction $x$ and translation direction $y$ for armchair SWCNTs.

While carbon nanotubes can be considered a seamless graphene cylinder, the sidewall curvature has a strong influence on electronic structure. Importantly, this leads to a pyramidalization of the C atoms, hence weakening the $\pi$-conjugation of the SWCNT. Each individual C atom exhibits partial $sp^3$ hybridization which requires a net rehybridization of $\sigma$, $\sigma^*$, $\pi$, and $\pi^*$ orbitals within the sidewall of the nanotube superstructure. Simplistically, this can be viewed as the partial incorporation of the atomic $s$ orbitals into the atomic $p_x$ orbitals [41]. Locally, each C atom residing in the cylinder exhibits partial $sp^3$ character with slight misalignment of $\pi$-orbitals between adjacent atoms [34–36, 39].

One useful strategy for quantifying curved $\pi$-conjugation in nanotubes is Haddon’s $\pi$-orbital axis vector (POAV)
method (Figure 2) [41–43]. In this description, the pyramidalization angle ($\theta_p$) is defined as

$$\theta_p = \theta_{\sigma\pi} - 90^\circ,$$

(2)

where $\theta_{\sigma\pi}$ is the angle between the $\pi$-orbital and the $\sigma$ bond. In ethylene (i.e., CH$_2$CH$_2$), $\theta_p = 0^\circ$ since the C=C double bond is planar. The extended carbon framework of graphite exhibits the same geometry as ethylene. In contrast, in methane (i.e., CH$_4$), $\theta_p = 19.5^\circ$ since the sp$^3$-hybridized C atom is pyramidal. The carbon network in diamond exhibits the same geometry as methane. In icosahedral fullerene C$_{60}$, $\theta_p = 11.6^\circ$, suggesting some deviation and planarity and, consequently, an increase in strain energy. This third allotrope of carbon exhibits varying degrees of pyramidalization depending on the size of the fullerene. In (5,5) SWCNTs, $\theta_p = 6.0^\circ$, consistent with a more planar superstructure. Carbon nanotubes typically exhibit a slight misalignment of the $\pi$-orbitals in adjacent C atoms depending on tube circumference. Overall, SWCNTs are generally more inert than the corresponding fullerenes of similar diameters [41, 44].

While useful, Haddon’s POAV analysis treats carbon atoms embedded in supramolecular carbon frameworks as independent entities [46, 47]. As a consequence, this pyramidalization approach only provides a description of mean reactivity of the vertex atoms but do not consider curvature of the C−C bonds themselves as predictive factors for chemical reactivity. As such, Li et al. introduced the concept of bond curvature $K$, which is characterized by directional curvature $K_D$ (corresponding to the arc curvature of C−C bonds) and its mean $K_M$ (corresponding to arc curvature of the vertex carbon atoms). For any given C$_a$–C$_b$ bond with bitemporal oblique angle $\theta$, the acute angle between the nanotube axis and the direction of the bond, $K_D$ and $K_M$ (for vertex atom $i$) are defined as

$$K_D = \frac{1}{2} \sum_{i=a,b} \left( K_{i1} \sin^2 \theta_i + K_{i2} \cos^2 \theta_i \right),$$

$$K_M = \frac{2}{\pi} \int_{0}^{\pi/2} \left( K_{i1} \sin^2 \theta_i + K_{i2} \cos^2 \theta_i \right) d\theta_i = \frac{1}{2} (K_{i1} + K_{i2}),$$

(3)

where $K_{i1}$ and $K_{i2}$ are the principle curvatures of carbon $i$. In spherical fullerenes (e.g., C$_{60}$), $K_D$ and $K_M$ are given:

$$K_D = K_M = \frac{1}{R_S},$$

(4)

where $R_S$ is the radius of the fullerene. For SWCNTs with radius $R$, $K_1 = 1/R$, $K_2 = 0$, $\theta_a = \theta_b = \theta$, and hence, $K_D$ and $K_M$ are given

$$K_D = \frac{\sin^2 \theta}{R},$$

$$K_M = \frac{1}{2R},$$

(5)

Li’s bond curvature analysis is also related to the pyramidalization angle as follows:

$$K_D = 2K_M \sin^2 \theta = \frac{4\theta_p}{r \sin^2 \theta},$$

$$K_M = \frac{1}{2R} = \frac{2\theta_p}{r},$$

(6)
where $r$ is the average C–C bond length (i.e., 1.42 Å). For spherical fullerenes,

$$K_M = K_D = \frac{2 \theta_p^s}{r},$$

where $\theta_p^s$ is the pyrimidalization angle for the vertex carbon atoms.

SWCNTs have a very large surface area, and as a consequence, inter-tube interactions are typically quite strong. Attractive forces either of a van der Waals or weak long-range covalent bonding on the order of 0.50 to 0.95 eV per nanometer of tube-to-tube contact have been observed. As a consequence, aggregation of SWCNTs typically leads to the production of hexagonally packed bundles or ropes [33, 37, 48, 49].

Carbon nanotubes are characterized by a very high aspect ratio (i.e., length per width) and extensive levels of electron delocalization [33, 34, 50]. Thus, SWCNTs exhibit strong confinement effects that result in a pronounced one-dimensionality and weak interaction between electrons and phonons. These macromolecules are ballistic conductors and exhibit two units of quantum conductance (i.e., $4e^2/h$), and the quantum resistance ($R_Q$) is defined as [11, 33, 50–52]

$$R_Q = \frac{\hbar}{4e^2} = 6.5k\Omega.$$ (8)

As such, mean free paths on the order of a micron have been suggested [34, 50, 53].

Chemical functionalization of carbon nanotubes can easily disrupt the extended conjugation and reduce the electrical conductivity along the axis of the tube. In particular, covalent modification of the sidewalls of carbon nanotubes has been achieved [3] via strategies including tandem fluorination/nucleophilic substitution [54–56], ozonolysis [57, 58], Diels–Alder cycloaddition [59, 60], osmylation [61], hydroboration [62], dissolving metal reduction (Billups reaction) [63], carbene addition [64], nitrene addition [65], dipolar cycloaddition of azomethine ylides [66], vinyl carbylation via zwitterionic intermediates [67, 68], other electrophilic oxidations [69], radical alkylation [64, 70], perfluoroalkylation [71, 72], and arylation [73]. Current technologies suffer from low reactivity and/or poor selectivity. Additionally, characterization of the functionalized SWCNT products remains a significant challenge.

Substitutional doping of carbon nanotubes is an alternative for electronic tuning [74]. In this case, a single C atom on the sidewall of a SWCNT is substituted with another atom, resulting in the production of a hetero-SWCNT (HSWCNT). Nitrogen- and boron-doping are among the most popular and have both been achieved [75]. Traditionally, N- and B-doped SWCNTs can be prepared via thermal treatment [76], chemical vapor deposition [77], laser ablation [78], and the arc method [79], but generally with poor control of doping position and concentration [74, 75]. To address these concerns, Srivastava et al. [80] proposed that a free gas-phase neutral N atom, if brought into close vicinity with a vacancy in the carbon backbone, could induce a selective substitution process to occur. Later, our group proposed the use of NO as a nitrogen source [81] by interaction with the so-called 5-1DB defects [82, 83] (i.e., a single vacancy defect site that contains one five-membered carbocycle and a single C atom with one dangling bond) that can be induced by ion and electron radiation [83, 84].

For substitutional N-doping, calculations have revealed that N-doped SWCNTs display only minimal geometric change in comparison to their undoped SWCNT analogs [85]. By substitution of a C atom with a B or N atom impurity, quasibound states consisting of $p$-orbitals are formed below and above the Fermi energy, respectively [86],
in analogy to $p$- and $n$-type semiconductors. This is because boron has one less electron than carbon, while nitrogen has one more electron [75]. In B-doped nanotubes at low amounts of doping, the mean-free path decreases linearly with dopant concentration, according to the Fermi golden rule [87]. Additionally, mean-free path scales linearly with nanotube diameter. At 1.0% of doping, mean-free paths of 175–275 nm for B-doped nanotubes with diameters 17–27 nm have been predicted (cf. 220–250 nm in doped multi-walled nanotubes [88]). The Kubo formula for conductance of a device, $G(E, L_{\text{dev}})$, is given:

$$G(E, L_{\text{dev}}) = \frac{2e^2 n(E)D_E(\tau_{\text{dev}})}{L_{\text{dev}}} ,$$

(9)

where $n(E)$ is the density of states per length at energy $E$ and $\tau_{\text{dev}}$ is the time required for the electronic wave to travel distance $L_{\text{dev}}$; hence, $D_E(\tau_{\text{dev}})$ is the diffusion coefficient [87]. In N-doped nanotubes, for a metallic SWCNT with a diameter of 1 nm, an energy level for the N atom can be located several hundred meV below the first van Hove singularity of the $\pi^*$-band [86, 89]. For a semiconducting congener, the nitrogen state lies 150–200 meV below the conduction band [75]. However, electron backscattering can complicate this simple description in some cases [86, 90].

The doping of the sidewall of SWCNTs with transition metals, however, remains to be achieved [91–95], despite the fact that the closely related transition metal-doped fullerenes have been synthesized and characterized [96–103]. Pt-, Ir-, Rh-, La-, Sm-, Sc-, and Y-doped fullerenes have been prepared via laser ablation or ionization, typically detected by mass spectrometry. The mechanism of formation is believed to involve formation of a fullerene-transition metal adsorbate complex, followed by insertion into the carbon framework [104]. Additionally, the synthesis of second- and third-row transition metal-doped fullerenes has been predicted to be attainable via reaction of the corresponding transition metal trichloride (or dichloride) in the presence of chlorine gas (Cl$_2$) and buckminsterfullerene (C$_{60}$) [105]. Theoretical studies also provide insight into the electronic properties of transition metal-doped fullerenes [106–109]. In general, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in transition metal-doped fullerenes decreases in comparison to the parent fullerene upon introduction of a transition metal atom into the cage [109], resulting in higher conductivity and reactivity [106], and hence suggests similar effects for nanotubes.

Our work in SWCNTs and their substitutionally doped analogs (i.e., HSWCNTs) is driven from a fundamental interest in the ability of the unique chemical reactivity of these carbon allotropes. In particular, defected [91, 110–112] and doped nanotubes [35, 36, 45, 110, 113, 114] have been the focus of our attention. Since nanomaterials have such great potential for application in biological systems, sensory technology, electronics, and catalysis, their fundamental chemistry warrant further investigation.

It is worthwhile at this point to discuss the toxicology of SWCNTs at the nanolevel [115–120]. It is commonly held that the entry of nanosized particles into biological systems is dangerous due to the ability of these molecules to persist indefinitely [121] because they do not typically undergo metabolism by macrophages. In reality, intertube interactions and bundle formation depends strongly on particle size, surface charge, and surface area. Consequently, agglomeration of nanoparticles and their diffusion through physiological environments are not easy to predict. In fact, recent efforts have shown that SWCNTs functionalized on the surface with carbonyl (C=O), carboxyl (COOH), and hydroxyl (OH) groups exhibit higher levels of cytotoxicity and can induce cell death either after contact with cell membranes or following internalization [122]. Functionalization with ammonium cations, however, can lead to enhanced clearance rates [123]. The main mode of toxicity in organisms on a macroscale is believed to be oxidative stress induced by the generation of reactive oxygen species (ROSs) [116, 117, 124–126]. The mechanism of action involves light-induced formation of electron-hole pairs and generation of unpaired electrons that can oxidize molecular oxygen ($O_2$) to superoxide ($O_2^-$). Other electron-active groups can also contribute to the production of superoxide due to defects or surface coatings [116, 117]. Although nature has evolved enzymes (e.g., superoxide dismutase, glutathione [127]) to counteract the effect of ROSs, accumulation over extended periods of time can force cells to respond by more drastic measures [124, 125, 127]. Numerous examples of carbon nanomaterial cytotoxicity have been reported, including work done on human skin fibroblasts [128], macrophages [129, 130], and developing zebrafish embryos [131]. Researchers have also demonstrated that carbon nanotubes can cause interstitial fibrosis [132] and pulmonary toxicity [121, 133] in rat lungs and increase platelet-derived growth factor (PDGF) messenger RNA (mRNA) levels significantly [132]. Clinically relevant toxicity data remains sparse [117], however, and several recent accounts suggest that low levels of nanosized carbon do not trigger immunological or inflammatory reactions [122] and may persist in mice for up to four months without any observable toxicity [134].

Nanotoxicity aside, nanotubes may find potential uses in therapy. For example, consider the interaction between SWCNTs and nitrogen monoxide (NO). Although nitrogen is one of the most important elements in biological systems, NO is known as being the toxic culprit for destroying ozone ($O_3$), causing cancer, and fostering acid rain. However, it plays a critical role at the interface of neuroscience, physiology, and immunology. Nitrogen monoxide was named “Molecule of the Year” in 1992 after its biosynthesis in mammalian cells, and its physiological relevance was recognized in the late 1980s [136, 137]. In fact, NO acts as a biological signaling molecule in the body and is important for learning and memory [138], blood pressure regulation [138, 139], skin homeostasis [140], inflammation [141], and carcinoma metastasis [142]. The biosynthesis of the gaseous free radical NO is achieved via a five-electron oxidation of arginine (Figure 3) [135, 136]. Physiological NO can inhibit metabolic pathways directly by binding to transition metal centers [143], as well as combine with molecular oxygen to give other ROSs including hydroxyl radicals, nitrogen
dioxide ($N_2O_4$) [137], and peroxynitrite (ONOO$^-$) [136, 138, 143]. If future nanodevices will be implanted into biological systems, it may interact with the biocycles of NO. Thus, the ability to adsorb NO would be important because it would reduce its concentration, which can be beneficial or dangerous depending on the site of activity. The controlled release of NO has recently attracted attention of researchers for antithrombotic activity [144], for instance. Indeed, chemically designed drugs (Figure 4) [136], zeolites [144, 145], and even Pt nanoparticles [146] may find applicability in NO homeostasis. Carbon nanotubes would represent an alternative strategy for controlling physiological NO.

We envisioned that doping the sidewall of SWCNTs with a transition metal would provide a unique opportunity for interacting with and binding small biologically relevant molecules such as NO. This hypothesis is based on the known ability of metal surfaces and discrete organometallic complexes to coordinate small molecules via the $d$ orbitals of the transition metal. Additionally, we imagined that transition metal-doped SWCNTs would exhibit electronic properties distinct both from the undoped SWCNT and B- and N-doped SWCNTs that would enhance its potential for application in nanoelectronics. For example, these nanomaterials may act as sensors by monitoring observed conductance as a function of adsorption of small gas molecules [147, 148]. Designing new sensorolgy technology for detecting NO would be important because it would reduce its concentration, which can be beneficial or dangerous depending on the site of activity. The controlled release of NO has recently attracted attention of researchers for antithrombotic activity [144], for instance. Indeed, chemically designed drugs (Figure 4) [136], zeolites [144, 145], and even Pt nanoparticles [146] may find applicability in NO homeostasis. Carbon nanotubes would represent an alternative strategy for controlling physiological NO.

In this review, we will highlight results from our own studies on the structure and electronic properties of substitutionally doped SWCNTs and their proposed synthesis. In addition, the chemical reactivity of HSWCNTs with small gas molecules will be discussed. The catalytic activity of transition metal-doped SWCNTs will also be described. Our investigative efforts constitute preliminary analyses toward a microscopic understanding of the biological roles of carbon-based nanomaterials and the development and discovery of new functional materials with exciting applications in the real world.

### 2. Substitutional Doping of SWCNTs

#### 2.1. Models and Computational Details

The (5,5) armchair metallic SWCNT and (5,0) zigzag SWCNT were used as models for all computations. Natural bond orbital (NBO) analysis was accomplished with Gaussian NBO Version 3.1 [155, 156] to obtain the frontier molecular orbitals (FMOs): the HOMO and the LUMO. Pioneered by Fukui and collaborators [157–161], the FMO analysis offers a powerful (albeit simple) understanding of chemical reactivities. Density of states (DOS) and local DOS (LDOS) studies were performed using PyMOLyze [162]. All other calculations were done with the Gaussian 03 quantum chemical package [163]. The Hessian was evaluated for all optimized structures to verify the nature of the stationary points on the potential energy surface. Both spin-restricted and spin-unrestricted optimizations yielded the same results for all ground-state complexes examined.

To study the substitutional doping of SWCNTs, we proposed that introduction of a single defect could provide a reactive site for atom transfer reagents (e.g., NO, O$_3$). A chemical reaction would thus provide a means of selective doping with a noncarbon atom. For our study of defected SWCNTs with NO [81], a (5,5) segment containing two hundred C atoms and twenty capping H atoms was chosen ($C_{200}H_{20}$). A single vacancy was created by removal of a single C atom, yielding a metastable conformation with three dangling bonds. Geometry optimization was achieved sequentially with the semiempirical MNDO-PM3 method [164], followed by the hybrid Hartree-Fock/density functional theory (DFT) method B3LYP [165–167] with Pople’s 6-31G basis set [168–171]. A two-layer ONIOM (our own N-layered integrated molecular orbital and molecular mechanics) model [172] was used for our calculations. The nine-membered ring surrounding the defect was considered the chemically active region and modeled with a $C_9H_8$ fragment as the higher layer treated at the B3LYP/6-31G(d) level of theory. All other C atoms in the lower layer were treated by the universal force field (UFF) [173]. For our study of defected SWCNTs with O$_3$ [111], a (5,5) segment containing one hundred and twenty C atoms and twenty capping H atoms was chosen ($C_{120}H_{20}$). A single vacancy was created analogously. Geometry optimization was achieved sequentially with the semiempirical AM1 method [174–176], followed by B3LYP [165–167] with Pople’s 6-31G basis set.
The static quantum mechanical calculations double- 
[168–171]. Although O₃ is a multiconfigurational species, 
DFT is able to accurately describe this system because 
of the incorporation of the exchange-correlation effects 
[61, 177, 178]. The static quantum mechanical calculations 
were confirmed by comparison to an atom-centered density 
matrix propagation- (ADMP-) [179–181] based ab initio 
molecular dynamics (AIMD) simulation.

For our study of other main group element-doped and 
transition metal-doped SWCNTs [110], a C₇₀H₃₀ fragment 
terminating with H atoms was chosen. A single C atom was 
removed from the sidewall and replaced with a heteroatom 
(i.e., Sn, Se, Te, Ni, Pd) to give C₆₉H₂₀Sn, C₆₉H₂₀Se, 
C₆₉H₂₀Te, C₆₉H₂₀Ni, and C₆₉H₂₀Pd, respectively. DFT calculations 
were performed using B3LYP [165–167] with the relative- 
core pseudopotential (ECP) of Hay and Wadt (LANL2) 
[182]. Geometry optimization was achieved sequentially 
with B3LYP using the smaller LANL2MB basis set, followed 
by LANL2DZ [183]. For C₆₉H₂₀Pt, the exchange- 
correlation functional of Perdew, Burke, and Ernzerhof (PBEPBE) 
[196] was applied using the same basis 
sets. Model systems PtMe₃⁺, PtPh₃⁺, Pt-doped phenalen, Pt-doped corannulene, and Pt-doped C₄₂ fullerene 
were treated similarly. Note that there are two distinct structural 
isomers of Pt-doped C₄₂ fullerene, one in which the Pt 
atom substitutes a C atom at the junction between three 
 pentagons (PPP isomer) and the other in which the Pt atom 
substitutes a C atom at the junction between a hexagon 
and two pentagons (HPP isomer). NMR chemical shifts (δ) 
were calculated using the gauge-independent atomic orbital 
(GIAO) method [197–199]. For the study of catalytic Diels- 
Alder reactions between maleic anhydride and cyclopenta- 
diene, we also compared our hypothetical organoplatinum 
Lewis acids with traditional Lewis acids (e.g., AlCl₃, AlMe₃, 
BF₃, BCl₃, BBr₃, SnCl₄, TiCl₄).

Figure 4: Clinically used NO donor drugs [136].

The isoelectronic transition metal-doped single-walled 
boron nitride nanotube (BNNT) and its undoped analog 
was also studied for comparison [200]. In fact, our calculations 
demonstrate that atomic Pt can interact with either pristine 
or Stone-Wales-defective (5,5) BNNTs to give Pt-doped 
BNNTs. A truncated (5,5) BNNT containing forty-five B and 
N atoms and twenty capping H atoms was chosen as the 
model (B₄₅N₄₅H₂₀). DFT calculations were performed using 
B3LYP/LANL2MB, followed by LANL2DZ [183] with 
Hay and Wadt’s relativistic ECP LANL2 [182]. Model systems 
PtMe₃⁺, PtPh₃⁺, Pt-doped phenalen, Pt-doped corannulene, and Pt-doped C₂₄ fullerene 
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isomers of Pt-doped C₂₄ fullerene, one in which the Pt 
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Lewis acids with traditional Lewis acids (e.g., AlCl₃, AlMe₃, 
BF₃, BCl₃, BBr₃, SnCl₄, TiCl₄).

2.2. Defected SWCNT Rods. A single vacancy along the 
backbone of a (5,5) SWCNT rod C₂₀₀H₂₀ can be formed via 
removal of a single C atom that can be induced by external 
irradiation [83, 84]. In our model system, this yields a defected 
SWCNT with molecular formula C₁₉₉H₂₀ that undergoes a 
structural rearrangement to yield a structure containing one 
five-membered carbocycle and a single C atom with one 
dangling bond (i.e., the 5-1DB defect). The single C atom 
that protrudes to the exterior of the sidewall surface of the 
SWCNT is referred to as the active carbon atom (C₁). Nine 
C atoms surrounding the active carbon atom constitute the 
entire 5-1DB defect (Figure 5). The hexagonal lattice of all 
other C atoms in the nanotube sidewall remains relatively 
unaffected. Because the active carbon atom remains outside 
the SWCNT superstructure, enhanced chemical reactivity 
with incoming molecular or atomic species should be 
possible due to coordinative unsaturation, as well as a smaller
steric hindrance. Single-point calculations revealed that the HOMO–LUMO gap decreased from 1.38 to 0.84 eV upon the introduction of the defect, suggesting a destabilization of the HOMO and stabilization of the LUMO by formation of the 5-1DB defect. The HOMO contains a large contribution from the lonepair of electrons on the active carbon atom and the π-bonds of the other atoms within the nine-membered ring highlighted in Figure 5(d). Using a truncated C9H8 fragment with fixed geometry, FMO analysis revealed that this smaller model can be used to represent most of the chemical properties of the defect. Introduction of the vacancy defect also resulted in several small changes in the DOS (Figure 6).

2.3. Substitutional N-Doping of SWCNTs via Chemical Reaction of Defected SWCNTs with NO. Since the 5-1DB defect possesses an active C atom, we were intrigued about the possibility of performing chemical reactions between defected SWCNTs and reactive small molecules [81]. In particular, nitrogen monoxide caught our attention due to its biological relevance (vide supra). NBO analysis of the defected SWCNT revealed that the active carbon atom contains an sp2.01-orbital with 1.51 electrons and a p-orbital with 0.51 electrons. The overall charge on C1 is 0.149. Free NO, on the other hand, exhibits polarization, where the O atom bears a charge of −0.181.

Our ONIOM model predicts an electrostatic interaction between the defected SWCNT and NO (Figure 7). First, the O-end of the nitrogen monoxide molecule attacks the active carbon atom C1, producing a heterocycle INT1 containing an N−O bond. This is the rate-limiting step of the N-doping process and requires only a mere 8.6 kcal/mol. This type of reaction results from the interaction of a singly-occupied molecular orbital of NO and the HOMO of the SWCNT. Subsequently, the N atom undergoes insertion into the C2−C3 bond to expand the pentagon via a three-membered-ring transition state to liberate INT2. C1−N bond formation occurs with concomitant cleavage of the
C1–O bond to give INT3. The N-oxide radical (C199H20NO) that results is formally an N-doped SWCNT that has undergone pyramidalizing oxygenation, where the N atom has filled the single vacancy where a carbon atom was removed.

In the presence of another equivalent of NO, the SWCNT can react a second time. The optimized geometry of INT3 reveals an N–O bond length of 1.41 Å with a partial charge of −0.574 residing on the O atom. The second molecule of NO interacts simultaneously with C1 and O1 through the N atom and via a four-membered-ring concerted, asynchronous transition state liberates one molecule of nitrogen dioxide (NO2) and the N-doped SWCNT product (C199H20N). This product is 78.3 kcal/mol more stable than the reactants and suggests that the net reaction of NO with C199H20 is thermodynamically feasible. Formally, NO acts as a reducing agent by breaking the weak N–O bond of INT3.

In comparison to the perfect and pristine SWCNT rod (C200H20), the N-doped HSWCNT exhibits a decreased HOMO–LUMO gap of 0.74 eV (cf. 1.38 eV for the undoped SWCNT and 0.84 eV for the defected SWCNT). Geometrically, the N atom is situated slightly above the nanotube circumference (Figure 8). The N atom bears a charge of −0.325, whereas the neighboring C atoms display charges of approximately 0.20.

2.4. Substitutional O-Doping of SWCNTs via Chemical Reaction of Defected SWCNTs with O3. Having established an understanding of N-doping in defected SWCNTs, we turned our attention to the chemical reaction of vacancy defects with O3 [111]. O3 is a strong oxidizing agent that is capable of cleaving the C≡C double bonds of alkenes to generate two C=O bonds via the Criegee mechanism [201, 202]. In this reaction, O3 undergoes a [3+2] cycloaddition with the olefin, generating a five-membered ozonide. This intermediate rearranges to form a second ozonide takes place via the intermediacy of a carbonyl and carbonyl oxide. Since nanotube sidewalls consist of extended π-frameworks of C atoms, ozonization is presumably possible. Using a shorter C120H20 segment of a (5,5) armchair SWCNT and repeating the geometry optimization following removal of a single C atom gave a 5-1DB defect with similar geometry to our C199H20 system (vide supra). C1 was confirmed as the active carbon atom, bearing a positive charge of 0.10.

We considered ozonization of all C–C bonds exhibiting partial C≡C double bond character within the backbone of the defect. Of all the possibilities explored, the reaction manifold that is most possible involves direct interaction between O3 and the active carbon atom (Figure 9). A weak interaction between O3 and the SWCNT takes place first to form the physisorbed INT. Based on NBO analysis, 0.19 electrons have transferred from the SWCNT to O3. O3 and C1 then undergo a one-step oxygenation and loss of singlet dioxygen to liberate Product. The transition state (TS) involves a tightly bound four-membered ring in which bond between C1 and O1 gets shorter and is essentially barrierless from the starting materials (−0.3 kcal/mol). Product is formally a substitutionally O-doped SWCNT. The overall process is extremely exothermic (−88.7 kcal/mol). Additionally, relaxation of singlet O2 to triplet O2 results in further stabilization (−117.7 kcal/mol). AIMD simulations were conducted in which the O3 molecule was placed above the center of the nine-membered ring of the 5-1DB defect. At 300 K, our calculations confirm the spontaneous reaction between O3 and C1 in less than 50 fs.

Careful examination of Product reveals that the bonding between C1 and O1 is very strong, exhibiting a bond length of 1.21 Å (cf. 1.20 Å for a C=O double bond [203]). Thus, the structure of this product may be more accurately described as oxidation of C1 to a carbonyl functional group with minimal
2.5. Other Main Group Element-Doped SWCNTs. Based on these investigations, substitutional doping appears to be favored, where the dopant atom is situated to the exterior of the nanotube superstructure. To confirm this assessment, we used a truncated (5,5) SWCNT capped with H atoms (i.e., C_{70}H_{20}) and substituted a single C atom in the middle of the segment with a heteroatom (i.e., Sn, Se, and Te). We performed geometry optimization by considering both the possibility of external doping and internal doping (Figure 10) [110]. Our calculations are consistent with the proposal that exo-substitution is more energetically favored than the corresponding endo-HSWCNTs. Significant structural rearrangement is required for end-doping, and a larger buildup of positive charge is observed for the dopant atom (Table 1). FMO analysis revealed that electron density is largely localized at the dopant atoms themselves in the case of endo-substitution but is delocalized along the backbone of the nanotube in exo-substitution (Figure 11).

2.6. Transition Metal-Doped SWCNTs. Using the same approach as described above, we substituted a single C atom in the middle of a truncated (5,5) SWCNT model capped with H atoms (i.e., C_{70}H_{20}) and obtained geometries of both endo- and exo-substitution for both Ni and Pd substitutions. In agreement with our studies on main group element-doped SWCNTs, exo-substitution is more energetically favored and
Figure 8: Optimized geometry and FMOs of C$_{199}$H$_{20}$N. Orbital energies are in parentheses [81].

Figure 9: Optimized geometries (with distances in Å) and energy profiles (with energies in kcal/mol) for the reaction of the defected SWCNT with O$_3$ [111]. Legend: dark grey = carbon, light grey = hydrogen, red = oxygen.

Table 1: Binding energy and geometric data for main group element-doped SWCNTs [110].

<table>
<thead>
<tr>
<th>Dopant atom (X)</th>
<th>Adsorption mode</th>
<th>$E_{\text{elec}}$</th>
<th>$d(X-C)$</th>
<th>q(X)</th>
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<tr>
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</tr>
</tbody>
</table>

$^a$Relative electronic energy of stabilization (in eV).

$^b$Bond length (in Å) between X atom and adjacent C atoms.

$^c$Partial charge on X.
Two geometries of substitutional doping, namely (a) endo- and (b) exo-substitution. [110].

Figure 10: Two geometries of substitutional doping, namely (a) endo- and (b) exo-substitution. [110].

Table 2: Binding energy and geometric data for transition metal-doped SWCNTs [110].

<table>
<thead>
<tr>
<th>Dopant atom (X)</th>
<th>Adsorption mode</th>
<th>( E_{\text{elec}} )(^{a} )</th>
<th>( d(X-C) )(^{b} )</th>
<th>q(X)(^{c} )</th>
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<td>Endo</td>
<td>2.552</td>
<td>1.937, 2.022, 2.022</td>
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</table>

\(^{a}\) Relative electronic energy of stabilization (in eV).
\(^{b}\) Bond length (in Å) between X atom and adjacent C atoms.
\(^{c}\) Partial charge on X.

induces a smaller structural rearrangement of the atoms of the nanotube sidewall (Table 2) [110]. Interestingly, localization of positive charge is insignificant in endo-substitution. In contrast to main group element-doped SWCNTs, these transition metal-doped congeners exhibit localization of electron density as evaluated by analysis of their FMOs (Figure 12).

2.7. Pt-Doped SWCNT Rods with Fullerene Caps. We were interested in substitutional doping of SWCNTs with a transition metal, particularly with Pt because of its potential application as nanosensors and nanocatalysts. By constructing a (5,5) SWCNT rod capped with fullerene hemispheres (C\(_{170}\), Figure 13(a)), we noted that three different types of atom substitution were possible: (1) cap-end-doping to generate C\(_{169}\)Pt(ce) (Figure 13(b)), (2) cap-doping to generate C\(_{169}\)Pt(c) (Figure 13(c)), and (3) wall-doping to generate C\(_{169}\)Pt(w) (Figure 13(d)) [35, 36]. Geometry optimization reveals that the Pt atom typically prefers to protrude to the exterior of the nanotube sidewall, adopting a conformation in which the three adjacent C atoms are situated in a tripod-like fashion. This may be a result of the larger size of the Pt atom and is consistent to the conclusions of Sections 2.5 and 2.6.

At the BPW91/6-31G level of theory, C\(_{169}\)Pt(ce) is the most stable of the three isomers. The energies of C\(_{169}\)Pt(c) and C\(_{169}\)Pt(w) are 0.8 and 17.9 kcal/mol, respectively, above that of C\(_{169}\)Pt(ce). In all calculations, the singlet electronic state was found to be lower in energy than the triplet. Hence, the Pt-doped nanorods exhibit a singlet ground state. Because of the extended \( \pi \)-framework of the sidewalls, however, the triplet excited state is also accessible.

Figure 13(b) shows the optimized geometry, DOS, and LDOS of C\(_{169}\)Pt(ce). The bond length between the Pt and C atoms at the cap end is 2.01 Å (cf. 1.73 Å for an isolated PtC molecule [114]). A careful analysis of the geometry of this Pt-doped nanorod reveals that the pentagonal and hexagonal structure is significantly distorted as a result of Pt-doping [35, 36]. Evidently, C\(_{169}\)Pt(c) is very similar geometrically to C\(_{169}\)Pt(ce) (Figure 13(c)). The bond distance between Pt and the C atom of the cap pentagon is 1.97 Å, while the distances to the remaining two C atoms are 2.00 Å. We suspect that the low energy of C\(_{169}\)Pt(ce) is a result of geometric relaxation of cap strain via the doping process.

The presence of Pt 5d atomic orbitals has a clear impact on the electronic structure of the nanorod in comparison to the undoped nanorod as evaluated by the DOS calculations. In C\(_{169}\)Pt(ce), \( L_1 \) displays sharp peaks in the LDOS at the cap that are not present in the model C\(_{170}\) segment (Figure 13(a)). This suggests that weak \( p_x-d_z \) interactions between the Pt atom and adjacent C atoms are taking place. The LDOS of the sidewall remains relatively unchanged. Interestingly, a similar electronic structure is observed for C\(_{169}\)Pt(c) (Figure 13(c)).
In the case of the wall-doped C_{169}Pt(w), both the geometric and electronic structures differ from the cap Pt-doped SWCNTs. While the LDOS at the cap resembles that of the undoped C_{170} model, significant changes in the LDOS at the nanotube sidewall can be observed (Figure 13(d)). Particularly, the sharp peaks that result from the Pt doping are now present in L5 instead of at L1.

Molecular orbital analysis confirms our assessment of these hypothetical Pt-doped nanorods with DOS (Figure 14). Indeed, localization of electron density can be seen primarily, where the substitution of the C atom with the Pt atom has taken place. The HOMO−LUMO gaps of C_{169}Pt(ce), C_{169}Pt(c), and C_{169}Pt(w) are 0.30, 0.23, and 0.20 eV, respectively.

2.8. Pt-Doped SWCNT Rods with Hydrogen Caps. Using a shorter C_{69}H_{20}Pt model derived from a truncated (5,5) SWCNT capped with H atoms (i.e., C_{70}H_{20}) (Figure 15), we were able to obtain a geometry that is consistent with the wall-doped fullerene-capped C_{169}Pt(w) nanorod (see Figure 13(d)) [114]. The Pt−C distances are 1.94, 1.94, and 2.01 Å in this case, with the Pt atom situated in the middle of a tripodal structure. A positive charge of 0.83 is present on the Pt center. Surprisingly, the HOMO−LUMO gap increased to 0.74 eV (cf. 0.20 eV for C_{169}Pt(w)). Nonetheless, a clear analogy between the molecular orbitals (MOs) of our C_{69}H_{20}Pt model and the wall-doped C_{169}Pt(w) can be observed (Figure 16). This result suggests that using H atoms to cap the truncated nanotube instead of fullerene hemispheres still allows us to capture most of the chemical properties of the Pt-doped SWCNT.

2.9. Pt-Doped BNNT Rods with Hydrogen Caps. Having acquired preliminary understanding of the geometric and electronic structures of Pt-doped SWCNTs, we turned our attention to the isoelectronic Pt-doped boron-nitride nanotube (BNNT) [200]. Although the B−N couple is isoelectronic with the C−C bond, the difference in electronegativity between the B and N atoms leads to the formation of dipoles. B has an empty p orbital and is a coordinatively unsaturated trigonal plane, while N has a full octet. In planar structures, this implies that B acts as electron acceptors, while N acts as electron donors. These electronic differences have chemical implications. For example, although molecular borazine (B_{3}N_{3}H_{6}) is isoelectronic and isostructural to benzene and possesses aromaticity, it is susceptible to addition reactions.
and to both nucleophilic and electrophilic attacks. Hexagonal boron nitride (hBN), the BN analog of graphite, exhibits extraordinary mechanical hardness and chemical inertness, while carbon graphite is used as a lubricant. BNNTs and SWCNTs also differ in several key regards. Zigzag BNNTs exhibit a nonzero dipole moment because of alternating layers of B and N atoms. Their band gaps and electronic structures around the Fermi level are generally invariant to changes in nanotube diameter and chirality due to localized ionic B–N bonds. BNNTs are incombustible at high temperatures and retain the chemical inertness of hBN [200, 204]. As such, BNNTs can be readily applied in nanoelectronics with minimal purification.

Boron-nitride nanotubes exhibit natural defects that can be induced from mechanical fractures [205, 206]. Among all possible defects, Stone-Wales (SW) defects are of particular interest [207]. Defects consisting of a pentagonal-heptagonal-heptagonal-pentagonal structure are found to be more stable than their corresponding quadrilateral-octagonal-octagonal-quadrilateral structure, even though, in the former case, homoatomic B−B and N−N bonds are present [206].

We initiated our studies by building a truncated (5,5) BNNT model capped with twenty H atoms (B_{45}N_{45}H_{20}) (Figure 17). Pristine BNNT contains two nonequivalent B−N bonds: (1) vertical B−N bonds perpendicular to the longitudinal direction of the tube (with length 1.453 Å) and (2) slant B−N bonds (with length 1.455 Å). Consequently, there are two distinct Stone-Wales defective BNNT resulting from either a slant B−N bond rotation (SW1) or a vertical B−N bond rotation (SW2). The formation of pentagons and heptagons results in electronic destabilization in comparison to the perfect hexagonal lattice of B and N atoms in pristine BNNTs. The HOMO of the pristine BNNT segment is composed largely of delocalized $p_\pi$ orbitals on the B atoms, while the LUMO consists of the unoccupied $p_{\pi}$ orbitals of the B atoms. The HOMO−LUMO gap is 6.02 eV, rendering the BNNT a good insulator. By introduction of the Stone-Wales defects, electron density localization at the B−B and N−N bonds results in a decrease of the HOMO−LUMO gap (4.98 and 5.19 eV for SW1 and SW2, resp.).

While both pristine and SW-defective BNNTs can physisorb Pt atoms, substitutional doping may also be possible. Substitution of either a single N or B atom gives two different structures with molecular formula B_{45}N_{44}H_{20}Pt and B_{44}N_{45}H_{20}Pt that must be considered independently (Figure 18). Both products have doublet ground states. The product resulting from N-substitution (i.e., B_{45}N_{44}H_{20}Pt) exhibits a slight positive charge buildup on the Pt atom. Additionally, the $\alpha$-spin HOMO is comprised of Pt 5$d_6$s and 6$p$ orbitals and has an energy of $-3.67$ eV, making the Pt-doped BNNT a good electron donor. In contrast, the $\alpha$-spin LUMO is raised to $-1.74$ eV and displays lower reactivity toward nucleophiles. The $\beta$-spin HOMO is electronically similar to that of pristine BNNT, while the $\beta$-spin is more similar to the $\alpha$-spin LUMO of this Pt-doped BNNT (i.e., B_{44}N_{45}H_{20}Pt). The band gap is 1.9 eV and renders these nanomaterials semiconducting.

The product resulting from B-substitution (i.e., B_{45}N_{44}H_{20}Pt) exhibits net donation of 1.15 electrons from Pt to the extended backbone of the nanotube. Spin density is also delocalized on its three surrounding N atoms. The $\alpha$-spin HOMO now consists primarily of Pt 5$d$ orbitals, while the $\alpha$-spin LUMO is made of Pt 5$d$ orbitals and N $p_{\pi}$
3. Gas Adsorption onto Metal-Doped SWCNTs

3.1. Adsorption of Carbon Monoxide. Since discrete organometallic Pt complexes [184, 186] and metal surfaces [188, 189] are known to undergo coordination or adsorption of carbon monoxide (CO), we imagined that adsorption of CO onto a Pt-doped SWCNT would also be possible [114]. Although the C≡O triple bond is polarized slightly toward the C atom, we considered two possibilities for CO adsorption; namely, C-end adsorption (giving a CO-adsorbed HSWCNT) and O-end adsorption (giving an QC-adsorbed HSWCNT) were both considered (Figure 19).

Adsorption of CO onto a Pt-doped SWCNT resulted in the release of 41.23 kcal/mol for C-end adsorption and 6.98 kcal/mol for O-end adsorption (Table 3). In coordination chemistry, we describe this type of interaction as a dative bond, in which the lone pair of electrons on the C atom donates into a metal d-orbital, causing a backdonation to the π*-orbital of the adsorbate. This analysis suggests slight
Figure 14: Relevant FMOs for $C_{169}$Pt(ce), $C_{169}$Pt(c), and $C_{169}$Pt(w). Orbital energies are in parentheses [35, 36].

Figure 15: Optimized geometry of $C_{69}H_{20}Pt$ (a) perpendicular and (b) parallel to the nanotube axis [114]. Legend: dark grey = carbon, light grey = hydrogen, blue = platinum.

lengthening of the C≡O triple bond. In our system, geometry optimization revealed a slight elongation of the C≡O triple bond from 1.18 Å in the free gas to 1.19 Å and a net charge of $-0.12$ on the CO molecule. In comparison, the O-end-adsorbed HSWCNT showed a C≡O bond length of 1.18 Å and a net charge of $-0.02$ on the adsorbate. The HOMO–LUMO gap was 0.66 eV. Hence, coordination of CO depends strongly on the orientation of the interaction, since adsorption via the C atom exhibited a more pronounced effect on the electronic structure of the Pt-doped SWCNT than the corresponding O-end adsorption.

It is well known that Pt complexes can host up to six ligands in its coordination sphere. Consequently, we decided to explore the possibility of multiple adsorption. We successfully identified a structure in which two CO molecules have undergone coordination to the Pt center through C-end adsorption (Figure 20). The ($CO)_2$-adsorbed HSWCNT segment was formed with a further release of energy (36.83 kcal/mol per CO molecule) and displayed almost identical orientation of both adsorbates. In comparison to monoadsorption, the distance between the Pt atom and the C atom of CO increased to 2.00 Å, while the net charges on the adsorbates decreased to $-0.05$ per CO molecule [114]. For triple adsorption, we were unable to locate a structure in which three molecules were bound strongly to the Pt atom via C-end adsorption; instead, based on our studies, it appeared that a third additional molecule of CO could interact weakly with the nanotube itself (cf. 3.13 Å between the Pt atom and the C atom of CO) [113]. Structurally, this ($CO)_3$-adsorbed HSWCNT was similar to the corresponding ($CO)_2$-adsorbed HSWCNT. The overall process is energetically downhill from the bare Pt-doped SWCNT but uphill from the doubly adsorbed intermediate. Presumably, the steric bulk of the nanotube backbone precludes the possibility of triple adsorption, despite the fact that the Pt atom remains coordinatively unsaturated.

3.2. Comparison with Alkylplatinum Complexes. In light of the ability of a HSWCNT undergoing adsorption with CO [114], we investigated model alkylplatinum complexes
through DFT. We examined all possible trimethylplatinum species of formulae PtMe$_3$(CO)$_x^{+}$ with $x$ between 0 and 3 and $n$ ranging from −3 to 1 (Figure 21 and Table 4).

Based on the observed geometry and partial charge analysis (with a positive charge of 0.83 on the parent Pt-doped SWCNT), we chose PtMe$_3$(CO)$_2^{+}$ for comparison purposes. Interestingly, triple adsorption was possible in this case. The limitation of double adsorption for the nanotube is thus likely a combination of steric and electronic factors. Namely, due to the bulk of the supramolecular framework and a HOMO with decreased electron density in the vicinity of the Pt atom, adsorption of a third molecule of CO onto a (CO)$_2$-adsorbed HSWCNT was not possible (Figure 22).


Having explored CO adsorption, we considered NO next (Figure 23). Nitrogen monoxide has a doublet ground state, and it is its radical character that dictates its role in biology [136]. Although Pt surfaces are known to interact with NO [188, 209–211], its use as a ligand for transition metal complexes is much less general (although the related NO$^+$ and NO$^-$ find widespread usage). Since the NO adsorbate has an unpaired electron, spin selection rules dictate that the resulting nanotube-adsorbate complex must also have an electronic state of doublet. We will denote the use of singlet ground-state Pt-doped SWCNT as a starting material as doublet-$s$, while the corresponding reaction of the triplet excited-state Pt-doped SWCNT will be termed doublet-$t$. Quartet states are also possible. In all cases examined, the quartet spin state had higher energy than the doublet states (−46.97 and −56.49 kcal/mol for doublet-$s$ and doublet-$t$, respectively) [113]. The Pt center now bears a charge of 0.99, while the N atom exhibits a charge of −0.21 and the O atom, −0.18. The HOMO–LUMO gap increased to 0.84 eV. Multiple adsorption was also considered, but geometry optimization revealed that the interaction of two molecules of NO with the HSWCNT occurred in an unsymmetrical fashion. In this case, one of the O atoms of the adsorbates clearly points away from the nanotube (Figure 23). Adsorption of three NO molecules was not considered.

Another small molecule we investigated was NH$_3$, a common stabilizing ligand for a number of Pt complexes [212–214], including the famous chemotherapy drug cisplatin (i.e., (H$_3$N)$_2$PtCl$_2$). Heterogeneous Pt surfaces have also been shown to interact with this gas in the industrial oxidation of NH$_3$ to NO in the first step of nitric acid production [215]. Unlike CO and NO, however, there is no low-lying n$^*$-orbital for backbonding to occur. Our optimized geometry of an NH$_3$-adsorbed HSWCNT revealed that the adsorption energy was −31.79 kcal/mol and the HOMO–LUMO gap was 0.73 eV. The coordination of ammonia, however, appears to be weaker since the distance from Pt to N was 2.25 Å (Figure 20). A partial charge analysis revealed that a negative charge of −1.13 resided on the N atom, while positive charges of 0.44 were present on each of the H atoms in NH$_3$ and a net charge of 0.19. Overall, this implies that a net σ-donation appears to be occurring from the adsorbate to the SWCNT. Biadsorption of NH$_3$ onto the Pt atom of this HSWCNT was possible with an energy change of −57.10 kcal/mol.

**Figure 16:** Relevant MOs for ground-state C$_{60}$H$_{20}$Pt. Orbital energies are in parentheses [114].
(28.5 kcal/mol per NO molecule). In agreement with the observation for (CO)$_2$-adsorbed HSWCNTs, the energy released per molecule decreased presumably because of increased steric effects.

We then turned our attention to adsorbates that have no inherent polarity. If our Pt-doped nanotubes will be applied as nanosensors for gases [148, 150–152, 154], expansion of the scope to simple and unpolarized small molecules is critical. Additionally, activation of unfunctionalized molecules may be important for catalytic applications. N$_2$, in particular, has been the focus of much attention due to its role in the industrial fixation of nitrogen via the Haber-Bosch process [216]. Productive interaction between a transition metal and N$_2$ can take place via two orientations, namely, end-on binding (with the N atom acting as a σ-donor to the metal), which typically requires the metal to be low valent [217], and side-on binding [218]. To our surprise, the structures of Pt-doped SWCNTs with either end-on or side-on binding of N$_2$ converged to give a geometry with an end-on-binding motif. The energy released upon this adsorption was much less than the corresponding number for CO adsorption (−24.72 kcal/mol). This is not unexpected since the adsorbate is largely nonpolar in character and does not exhibit any natural electrostatic attractive forces to the positively charged Pt center. The observed N≡N distance was lengthened only slightly from 1.15 Å in the free gas to 1.16 Å in this complex (Figure 20). Interestingly, the net charge on the N$_2$ molecule was −0.14, which signifies a net donation of electrons from the Pt atom to the oncoming ligand. We were able to identify a doubly adsorbed complex as in the case of CO and NO. In this scenario, though, the energy released per molecule of N$_2$ (−21.96 kcal/mol) was much closer to that of single adsorption (−24.72 kcal/mol). One possible explanation for this observation is that the weaker interaction between Pt and the adsorbate results in a smaller steric repulsion between the two N$_2$ molecules. The calculated HOMO–LUMO gap for this complex was 0.81 eV.
3.4. Adsorption of Hydrogen Gas. It is clear that the incorporation of Pt into the sidewall of the SWCNT allows unique interactions with gases that are otherwise not possible. We decided to examine the possibility of side-on adsorption, first examining the interaction of a Pt-doped SWCNT with H$_2$ (Figure 24 and Table 5). Indeed, activation of H$_2$ with Pt has found tremendous application in organic synthesis with regard to the hydrogenation of alkenes and alkynes. Our Pt-doped SWCNT is unique in the sense that it sits between the two extremes of heterogeneous and homogeneous activation of small molecules.

Using the larger C$_{169}$Pt nanorods capped with fullerenes as our model system, we initially found that the location of the Pt substitution had a drastic effect of the adsorption of H$_2$ [35, 36]. In the case of both cap-doped HSWCNTs (i.e., C$_{169}$Pt(ce) and C$_{169}$Pt(c)), the net process appeared to be physisorption, with a relatively weak interaction between the Pt atom and the adsorbate. Only approximately 2.0 kcal/mol of energy was released. Additionally, the H–H bond distance was not significantly altered from that of free H$_2$ in these cases. However, we were surprised to find that C$_{169}$Pt(w) was able to interact strongly with H$_2$ and induce chemisorptions.
In this reaction, a formal oxidative addition of the Pt center is taking place via hemolytic H–H cleavage. The energy released for this process was close to 10.0 kcal/mol, almost five times that of physisorption on the cap-doped HSWCNTs. Here, the distance between the H atoms had increased to 1.70 Å.

In comparison, the smaller fragment (5,5) C_{69}H_{20}Pt nanotube segment also yielded a geometry similar to that observed for C_{169}Pt(w) [113]. Chemisorption was again the result, and we observed a 2.16 Å separation between the two H atoms. The energetic preference for this reaction was −11.32 kcal/mol for the ground state. The HOMO–LUMO gap was 0.70 eV, and single-point calculations revealed a charge of 0.77 on the Pt atom and −0.34 on the adsorbate.

A related study on the isoelectronic Pt-doped BNNTs was also recently reported [208]. Li et al. demonstrate that up to three equivalents of H_{2} can undergo physisorption to the Pt center.

3.5. Adsorption of Ethylene. The hydrogenation of alkenes and alkynes using transition metals as an activator also typically requires an interaction of the substrate with the surface. The simplest two-carbon alkene is ethylene (C_{2}H_{4}) and has been studied with regard to physisorption and chemisorptions [219].

Again, with the larger Pt-doped nanorod models, physisorption was observed to occur with Pt–C distances of approximately 2.30 Å. The strength of interaction as gauged by the length of the C=C double bond suggests a weaker adsorption at the caps (1.40 Å for C_{169}Pt(ce), 1.41 Å for C_{169}Pt(c)) than the sidewall (1.42 Å for C_{169}Pt(w)). Nonetheless, the effect of transition metal coordination is clear, since the double bond is elongated from the 1.35 Å bond distance observed in the free gas. A close analysis of the energy changes associated with the physisorption process reveals that C_{169}Pt(w) has the strongest interaction with C_{2}H_{4} [35, 36]. These distances are in agreement with those reported for the adsorption of ethylene onto an Ir-doped fullerene [97].

We also confirmed that a molecule of C_{2}H_{4} can interact with the Pt center of the H-capped HSWCNT [113]. The amount of energy released, however, was only −26.43 kcal/mol for the singlet electronic state, and the HOMO–LUMO gap increased to 0.88 eV. The observed C=C distance was 1.43 Å (Figure 24 and Table 5). A net negative charge of −0.25 on the adsorbate was found by NBO analysis.

3.6. Adsorption of Acetylene. Having completed the investigation of the adsorption of ethylene, we turned to acetylene (C_{2}H_{2}), a small gas molecule that plays a significant role in
Figure 20: Optimized geometries for end-on adsorbed HSWCNTs [114]. Legend: dark grey = carbon, light grey = oxygen, navy blue = nitrogen, red = oxygen, blue = platinum.
Table 3: Binding energy and geometrical data for nanotube-adsorbate complexes C_{69}H_{20}Pt(XY) with end-on binding motif [114].

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<th>( d(XY) ) c</th>
<th>q(Pt) d</th>
<th>q(XY) e</th>
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<td>N/A</td>
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<td>N/A</td>
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<td>0.85</td>
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<td>OC(_{2})h</td>
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<td>1.18</td>
<td>0.87</td>
<td>-0.02</td>
<td>-0.41</td>
</tr>
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<td>(CO(<em>{2}))(</em>{2})h</td>
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<td>1.19, 1.19</td>
<td>0.83</td>
<td>-0.05, -0.05</td>
<td>-0.49</td>
</tr>
<tr>
<td>N(_{2})h</td>
<td>Doublet-s</td>
<td>-46.97</td>
<td>1.91</td>
<td>1.24</td>
<td>0.99</td>
<td>-0.39</td>
<td>-0.39</td>
</tr>
<tr>
<td>N(_{2})h</td>
<td>Doublet-t</td>
<td>-36.49</td>
<td>1.91</td>
<td>1.24</td>
<td>0.99</td>
<td>-0.39</td>
<td>-0.39</td>
</tr>
<tr>
<td>ON(_{2})h</td>
<td>Doublet-s</td>
<td>-23.18</td>
<td>2.14</td>
<td>1.27</td>
<td>0.98</td>
<td>-0.37</td>
<td>-0.34</td>
</tr>
<tr>
<td>ON(_{2})h</td>
<td>Doublet-t</td>
<td>-32.71</td>
<td>2.14</td>
<td>1.27</td>
<td>0.98</td>
<td>-0.37</td>
<td>-0.34</td>
</tr>
<tr>
<td>(NO(<em>{2}))(</em>{2})h</td>
<td>Singlet</td>
<td>-69.94</td>
<td>2.10, 2.12</td>
<td>1.24, 1.24</td>
<td>0.99</td>
<td>-0.24, -0.28</td>
<td>-0.36</td>
</tr>
<tr>
<td>NH(_{3})i</td>
<td>Singlet</td>
<td>-31.79</td>
<td>2.25</td>
<td>N/A</td>
<td>0.92</td>
<td>0.18, 0.18</td>
<td>-0.48</td>
</tr>
<tr>
<td>NH(_{3})i</td>
<td>Triplet</td>
<td>-31.28</td>
<td>2.23</td>
<td>N/A</td>
<td>0.87</td>
<td>0.18</td>
<td>-0.50</td>
</tr>
<tr>
<td>(NH(<em>{3}))(</em>{2})i</td>
<td>Singlet</td>
<td>-57.10</td>
<td>2.27, 2.27</td>
<td>N/A</td>
<td>0.92</td>
<td>0.18, 0.18</td>
<td>-0.48</td>
</tr>
<tr>
<td>N(_{2})j</td>
<td>Singlet</td>
<td>-24.72</td>
<td>2.08</td>
<td>1.16</td>
<td>0.91</td>
<td>-0.14</td>
<td>-0.41</td>
</tr>
<tr>
<td>N(_{2})j</td>
<td>Triplet</td>
<td>-25.90</td>
<td>2.05</td>
<td>1.16</td>
<td>0.91</td>
<td>-0.18</td>
<td>-0.44</td>
</tr>
<tr>
<td>(N(<em>{2}))(</em>{2})j</td>
<td>Singlet</td>
<td>-43.91</td>
<td>2.16, 2.16</td>
<td>1.16, 1.16</td>
<td>0.93</td>
<td>-0.09, -0.09</td>
<td>-0.42</td>
</tr>
<tr>
<td>(N(<em>{2}))(</em>{2})j</td>
<td>Triplet</td>
<td>-41.68</td>
<td>2.16, 2.16</td>
<td>1.16, 1.16</td>
<td>0.89</td>
<td>-0.09, -0.09</td>
<td>-0.41</td>
</tr>
</tbody>
</table>

aTotal stabilization energy (in kcal/mol)
bDistance (in Å) between Pt and X of XY.
cDistance (in Å) between X and Y of XY.
dPartial charge on Pt.
eNet partial charge on XY.
fNet partial charge on the C atoms of the SWCNT adjacent to Pt.
g[20].
hXYn refers to an n X-end adsorbed HSWCNT fragment.
iEnd-on adsorption.

the chemical industry [191, 192]. In fact, the utilization of Pt surfaces for catalytic hydrogenation is known as an efficient strategy for the production of ethane [192, 220, 221]. Alkynes have also been shown to interact with transition metals both through weak donation of \( \pi \)-electrons of the adsorbate to the metal. In some circumstances, stronger interactions that result in the oxidative addition of the transition metal can liberate a metallocyclopropene organometallic complex.

We only considered the (5,5) Pt-doped SWCNT segment capped with H atoms for this investigation [113]. We found that the adsorption of \( \text{C}_2\text{H}_2 \) resulted in the liberation of 31.36 kcal/mol of energy for the ground state configuration and lengthened the C≡C distance from 1.23 Å in the free gas to 1.32 Å (Figure 24 and Table 5). The HOMO–LUMO gap was similar to ethylene adsorption at 0.88 eV. A net charge of –0.38 was detected for the alkyne adsorbate, while the Pt center bore a charge of 0.98. The separation between the Pt atom and either C atoms was approximately 2.15 Å. Based on these evidences, we can safely conclude that the chemical reaction of acetylene with a Pt-doped SWCNT results in the generation of a metallocyclopropene via a chemisorptive process. Furthermore, the terminal C–H bonds are no longer colinear with the C≡C bond but instead are bent. The adsorption process hence induces a rehybridization of the C atoms from \( sp^2 \) to almost \( sp^3 \).

4. Catalytic Applications of Metal-Doped SWCNTs

4.1. Lewis Acidity of Pt-Doped SWCNTs. Our previous work on Pt-doped SWCNTs revealed that these substitutionally doped nanostructures exhibit certain electronic similarities to alkylplatinum complexes such as PtMe\(_3^+\) [114]. We hence considered the use of HSWCNTs as Lewis acid
Table 4: Data for model alkylplatinum and nanotube-adsorbate complexes [114].

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta E^a$</th>
<th>$d$(PtC)$^b$</th>
<th>$d$(CO)$^c$</th>
<th>$q$(Pt)$^d$</th>
<th>$q$(CO)$^e$</th>
<th>$q$(C)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtMe$_3$</td>
<td>0</td>
<td>0.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtMe$_3$(CO)$^+$</td>
<td>-28.11</td>
<td>2.04</td>
<td>1.17</td>
<td>0.84</td>
<td>0.09</td>
<td>-2.13</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_2$$^+$</td>
<td>-55.41</td>
<td>2.05, 2.05</td>
<td>1.17, 1.17</td>
<td>0.79</td>
<td>0.14, 0.14</td>
<td>-2.34</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_3$$^+$</td>
<td>-81.90</td>
<td>2.05, 2.05, 2.05</td>
<td>1.17, 1.17, 1.17</td>
<td>0.74</td>
<td>0.17, 0.17, 0.17</td>
<td>-2.47</td>
</tr>
<tr>
<td>PtMe$_3$</td>
<td>0</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtMe$_3$(CO)</td>
<td>-41.19</td>
<td>1.93</td>
<td>1.19</td>
<td>0.68</td>
<td>-0.05</td>
<td>-2.71</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_2$</td>
<td>-63.47</td>
<td>1.96, 1.96</td>
<td>1.19, 1.19</td>
<td>0.75</td>
<td>-0.05, -0.05</td>
<td>-2.70</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_3$</td>
<td>-70.64</td>
<td>1.98, 1.98, 2.40</td>
<td>1.19, 1.19, 1.20</td>
<td>0.75</td>
<td>0.00, 0.00, -0.17</td>
<td>-2.65</td>
</tr>
<tr>
<td>PtMe$_3$$^-$</td>
<td>0</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtMe$_3$(CO)$^-$</td>
<td>-64.41</td>
<td>1.87</td>
<td>1.21</td>
<td>0.53</td>
<td>-0.17</td>
<td>-3.18</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_2$$^-$</td>
<td>-77.30</td>
<td>1.92, 1.93, 2.97</td>
<td>1.20, 1.21, 1.21</td>
<td>0.76</td>
<td>-0.27, -0.22, -0.22</td>
<td>-2.94</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_3$$^-$</td>
<td>0</td>
<td>-0.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_2$</td>
<td>-66.81</td>
<td>1.88</td>
<td>1.23</td>
<td>-0.15</td>
<td>-0.40</td>
<td>-3.20</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_3$</td>
<td>-86.15</td>
<td>1.91, 2.03</td>
<td>1.25, 1.25</td>
<td>0.65</td>
<td>-0.55, -0.56</td>
<td>-3.24</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_3$$^+$</td>
<td>-107.55</td>
<td>1.98, 2.00, 2.72</td>
<td>1.23, 1.24, 1.24</td>
<td>0.65</td>
<td>-0.43, -0.44, -0.45</td>
<td>-3.11</td>
</tr>
<tr>
<td>PtMe$_3$$^-$</td>
<td>0</td>
<td>-1.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtMe$_3$(CO)$^+$</td>
<td>-71.74</td>
<td>1.88</td>
<td>1.23</td>
<td>-1.12</td>
<td>-0.38</td>
<td>-3.19</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_2$$^+$</td>
<td>-93.82</td>
<td>1.91, 2.08</td>
<td>1.26, 1.26</td>
<td>0.08</td>
<td>-0.60, -0.73</td>
<td>-3.36</td>
</tr>
<tr>
<td>PtMe$_3$(CO)$_3$$^+$</td>
<td>-130.61</td>
<td>2.14, 2.15, 2.15</td>
<td>1.25, 1.26, 1.26</td>
<td>0.21</td>
<td>-0.55, -0.55, -0.55</td>
<td>-3.25</td>
</tr>
<tr>
<td>Pt-doped SWCNT$^8$</td>
<td>0</td>
<td>0.82</td>
<td></td>
<td></td>
<td></td>
<td>-0.41</td>
</tr>
<tr>
<td>CO-adsorbed HSWCNT$^8$</td>
<td>-41.23</td>
<td>1.97</td>
<td>1.19</td>
<td>0.85</td>
<td>-0.12</td>
<td>-0.43</td>
</tr>
<tr>
<td>(CO)$_2$-adsorbed HSWCNT$^8$</td>
<td>-73.67</td>
<td>2.00, 2.00</td>
<td>1.19, 1.19</td>
<td>0.83</td>
<td>-0.05, -0.05</td>
<td>-0.49</td>
</tr>
</tbody>
</table>

$^a$Total stabilization energy (in kcal/mol).
$^b$Distance (in Å) between Pt and C of CO.
$^c$Distance (in Å) between C and O of CO.
$^d$Partial charge on Pt.
$^e$Net partial charge on CO.
$^f$Net partial charge on the C atoms adjacent to Pt.

Table 5: Binding energy and geometrical data for nanotube-adsorbate complexes C$_{69}H_{20}$Pt(X$_2$) with side-on binding motif [113, 114].

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>X</th>
<th>Spin state</th>
<th>$\Delta E^a$</th>
<th>$d$(PtX)$^b$</th>
<th>$d$(XX)$^c$</th>
<th>$q$(Pt)$^d$</th>
<th>$q$(X)$^e$</th>
<th>$q$(C)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>N/A</td>
<td>Singlet</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
<td>0.82</td>
<td>N/A</td>
<td>-0.41</td>
</tr>
<tr>
<td>N/A</td>
<td>Triplet</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.84</td>
<td>N/A</td>
<td>-0.49</td>
</tr>
<tr>
<td>H$_2$</td>
<td>H</td>
<td>Singlet</td>
<td>-11.32</td>
<td>1.66, 1.68</td>
<td>2.16</td>
<td>0.77</td>
<td>-0.34</td>
<td>-0.33</td>
</tr>
<tr>
<td>H</td>
<td>Triplet</td>
<td>-9.02</td>
<td>1.66, 1.66</td>
<td>2.19</td>
<td>0.74</td>
<td>-0.34</td>
<td>-0.43</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>CH$_2$</td>
<td>Singlet</td>
<td>-26.43</td>
<td>2.31, 2.20</td>
<td>1.43</td>
<td>0.95</td>
<td>-0.25</td>
<td>-0.35</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>Triplet</td>
<td>-24.74</td>
<td>2.31, 2.30</td>
<td>1.42</td>
<td>0.92</td>
<td>-0.16</td>
<td>-0.37</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>CH</td>
<td>Singlet</td>
<td>-31.36</td>
<td>2.13, 2.10</td>
<td>1.32</td>
<td>0.98</td>
<td>-0.38</td>
<td>-0.34</td>
</tr>
<tr>
<td>CH</td>
<td>Triplet</td>
<td>-25.29</td>
<td>2.17, 2.15</td>
<td>1.30</td>
<td>0.92</td>
<td>-0.27</td>
<td>-0.31</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Total stabilization energy (in kcal/mol).
$^b$Distances (in Å) between Pt and each X of X$_2$.
$^c$Distance (in Å) between X and X of X$_2$.
$^d$Partial charge on Pt.
$^e$Net partial charge on X$_2$.
$^f$Net partial charge on the C atoms of the SWCNT adjacent to Pt.
Figure 21: Optimized geometries of alkylplatinum model compounds [114]. Legend: dark grey = carbon, light grey = carbon, red = oxygen, blue = platinum.

Catalysts [45]. To evaluate Lewis acidity, we considered three main parameters. First, since CO is known to coordinate to Pt atoms, we performed vibrational analyses for the C≡O stretch as an indicator for the level of backdonation from the metal center to the ligand. Second, the nuclear magnetic resonance (NMR) chemical shift ($\delta$) of the olefinic H in the $\beta$ position of an $\alpha,\beta$-unsaturated carbonyl compound, maleic anhydride, was evaluated. This strategy was first pioneered
by Childs and coworkers [222, 223] as an experimental and theoretical method for determining Lewis acidity. Compared to the uncomplexed maleic anhydride (MA), Lewis acid coordination is expected to generate a positive downfield shift of the proton resonance at the β position due to a deshielding effect (Figure 25). Hence, chemical shift difference (Δδ) is a direct measure of Lewis acidity. Third, we further envisioned that Pt-doped SWCNTs could also act as catalysts for the Diels-Alder reaction between maleic anhydride and cyclopentadiene (CPD), a [4+2] cycloaddition (Figure 26). This one-step reaction involves a concerted but asynchronous six-membered transition state via either an exo- or endo-pathways, generating two possible products, namely, the exo- and endo-adducts. We evaluated Lewis acidity based on rate enhancement, as well as selectivity between exo- and endo-products. Although subtle solvent effects have been noted in the literature [224–230], we did not consider these factors in our calculations.

To evaluate the Lewis acidity of Pt-doped SWCNTs, a series of model systems were considered, including PtMe₃⁺, PtPh₃⁺, Pt-doped phenaline, Pt-doped sumanene, Pt-doped corannulene, and Pt-doped C₂₄ fullerene. Particularly, Pt-doped C₂₄ fullerene can exist as either one of two isomers, namely, Pt-substitution at a pentagon-pentagon-pentagon junction (PPP isomer) or a hexagon-pentagon-pentagon junction (HPP isomer). As mentioned above, the cationic PtMe₃⁺ was observed to bear the most similarity to Pt-doped SWCNT in terms of geometry, localized charge, and ability to bind CO as a ligand [114]. The other model systems chosen for this investigation include aromatic ligands (PtPh₃⁺) and cyclic carbon frameworks. Buckybowl-type architectures [231, 232] are derived from smaller pieces of C₆₀ fullerene, sumanene, and corannulene, respectively. The geometrically confined C₂₄ skeleton was also explored as a means of studying the direct effect of curvature and π-conjugation on the Lewis acidity of Pt-doped SWCNTs.

We chose a segment from a (5,0) Pt-doped SWCNT capped with ten H atoms with molecular formula C₂₉H₁₀Pt. We obtained this structure via substitution of a single C atom in the middle of the segment with a Pt atom, followed by geometry optimization. Not surprisingly, bare (5,0) Pt-doped SWCNTs exhibited a geometry similar to (5,5) Pt-doped SWCNTs in which the Pt atom protrudes to the exterior of the nanotube sidewall (Figure 27) [45], likely because of the larger atomic radius of Pt and longer Pt–C bonds [113, 114]. The three neighboring C atoms are arranged in
2.12 Å

(a) Side view of (NO)$_2$-adsorbed Pt-doped SWCNT perpendicular to the nanotype axis

(b) Side view of (NO)$_2$-adsorbed Pt-doped SWCNT perpendicular to the nanotype axis

Figure 23: Optimized geometry of (NO)$_2$-adsorbed HSWCNT. Orbital energies are in parentheses [113]. Legend: dark grey = carbon, light grey = hydrogen, navy blue = nitrogen, red = oxygen, blue = platinum.

2.16 Å

(a) H$_2$ adsorption

(b) C$_2$H$_4$ adsorption

(c) C$_2$H$_2$ adsorption

Figure 24: Optimized geometries for side-on adsorbed HSWCNTs [113]. Legend: dark grey = carbon, light grey = hydrogen, blue = platinum.

a tripodal fashion around the pyramidalized Pt center and exhibit a significant deviation from planarity ($\sum = 292.2^\circ$, cf. $\sum = 360^\circ$ for a planar hybridization scheme) [45]. PtMe$_3^+$ and PtPh$_3^+$ both display less pyramidalization, with $\sum = 297.5^\circ$ and 315.4$^\circ$, respectively. This is because the carbon ligands of these organometallic complexes are not tied back as in the case of the Pt-doped SWCNTs. The Pt-doped analog of phenaline, a segment derived from an idealized graphene sheet, exhibited high levels of buckling ($\sum = 279.6^\circ$). In contrast, the fullerene model systems, Pt-doped sumanene, Pt-doped corannulene, and Pt-doped C$_{24}$ (PPP and HPP isomers), are all more highly pyramidalized than any of the other systems investigated (i.e., $\sum < 270^\circ$) (Figure 28).

A brief analysis of the FMOs revealed a significant interaction between metal d orbitals and the delocalized C framework that depended strongly on the $\pi$-curvature (Figure 29). Notably, the amount of electron density present on the Pt center is small in both Pt-doped fullerenes (HPP isomer) and SWCNTs in comparison to the other model complexes studied.

4.2. Evaluation of Lewis Acidity by Adsorption of CO. We decided to examine the coordination of CO via C-adsorption to alkyl- and arylplatinum complexes as a gauge of Lewis acidity (vide supra). As mentioned previously, the binding of CO involves donation of the nonbonding $\sigma$ electrons of the C atom to the appropriate unoccupied metal d orbital. This stimulates the metal center to backdonate electrons to the $\pi^*$ orbital of the adsorbate and causes weakening of the C≡O bond [233–235]. Specifically, a lower C≡O stretching frequency implies lower Lewis acidity, and vice versa. Our calculations confirm that binding of CO and the formation of organoplatinum–CO complexes are energetically favorable. Indeed, simple alkyl- and arylplatinum complexes have a tendency to deplete electron density from the adsorbate (Table 6). Surprisingly, the Pt-doped (5,0) SWCNT model system demonstrated net donation of electron density from the CO molecule, contrasting our previous work that showed net backdonation in Pt-doped (5,5) SWCNTs [113, 114].

By analysis of the vibrational frequencies of CO molecules bound to alkyl- and arylplatinum complexes, the predicted trend of Lewis acidity is as follows [45]:
(5,0) Pt-doped SWCNTs are most similar to fullerene models, Pt-doped corannulene, and Pt-doped C_{24}, in their strong affinity for CO. Although these particular organoplatinum models exhibit less positive charge buildup on the Pt atom than the others, the extended carbon frameworks and higher levels of π-conjugation seem to increase the ability to backbond to incoming ligands.

This leads to very tight Pt–CO interactions (∼2.00 Å). Pt-doped phenaline appears to be more Lewis acidic (ω_{C\equiv O} = 2050.3 cm^{-1}) than the other arylplatinum complexes. In comparison to both Pt-doped nanotubes and fullerenes, this arylplatinum complex exhibits lower levels of π-curvature in the C backbone and increased levels of planarity. This observation implies that distortion of adjacent p_π orbitals imposed by curvature decreases the effective Lewis acidity in Pt-doped supramolecular carbon frameworks. PtMe_3^{+} and PtPh_3^{+} exhibit the weakest interaction with CO molecules (d(Pt–C) ∼ 2.11 Å), in agreement with the observation that decreased π-curvature and π-conjugation lead to an increase...
Figure 27: Optimized geometry of model (5,0) Pt-doped SWCNT segment [45]. Legend: dark grey = carbon, light grey = hydrogen, blue = platinum.

Figure 28: Optimized geometries of model alkyl- and arylplatinum complexes [45].
in Lewis acidity and weaker backbonding. Based on this hypothesis, we expect that Pt-doped phenaline, PtMe$_3^+$, and PtPh$_3^+$ should be superior to organoplatinum complexes with higher $\pi$-curvature in their ability to catalyze chemical reactions (vide infra).

4.3. Evaluation of Lewis Acidity by Complexation with Maleic Anhydride. In 1982, Childs and coworkers suggested a general method for evaluating Lewis acidity by NMR analysis of an $\alpha,\beta$-unsaturated carbonyl compound/Lewis acid complex [222, 223]. Indeed, the chemical shift $\delta$ of the olefinic

Figure 29: FMOs of model alkyl- and arylplatinum complexes, Pt-doped fullerene and SWCNT. Orbital energies are in parentheses [45].
H in the β position is expected to shift downfield (i.e., higher ppm). We also analyzed bond lengths as indirect measures of Lewis acidity, since a more Lewis acidic species should cause more significant weakening of the C1=O bond, strengthening of the C1−C2 bond, and weakening of the C2=C3 bond (i.e., the bond between the α and β carbon atoms).

Our calculations confirmed that complexation between maleic anhydride and Lewis acids typically causes a downfield shift of the β-H 1H NMR signal (Table 7) [45]. Surprisingly, (5,0) Pt-doped SWCNT and Pt-doped corannulene result in a decreased chemical shift of the β-H, implying that the charge-separated resonance structure (Figure 25) is less important than in the free maleic anhydride molecule.

Figure 30: LUMO of Lewis acid/maleic anhydride complexes. Orbital energies are in parentheses [45].
This is likely due to larger steric hindrance toward the productive coordination of maleic anhydride to the Pt atom. Otherwise, the Lewis acidity of alkyl- and arylplatinum model complexes appear to decrease the chemical shift more than traditional Lewis acids ($\Delta\delta \sim 0.5$ ppm), except for Pt-doped fullerenes. Hence, our organoplatinum model complexes derived from substitutional doping of a Pt atom are in fact strong Lewis acids. Also, we demonstrated that Lewis acid/Lewis base pair formation decreases the C1–C2 bond length and increases C1=O and C2=C3 bond lengths. This is because contribution from the resonance structure involving charge separation gains more weight as a result of the complexation. Accordingly, reactivity at C2 and C3 towards electrophiles and nucleophiles, respectively, presumably increases as a result of this binding due to charge separation in the maleic anhydride starting material. By bond-length analysis, our alkyl- and arylplatinum complexes appear to be roughly equivalent to traditional Lewis acids in
arylplatinum complexes, PtMe$_3^+$ and PtPh$_3^+$, deviations than with the corresponding simple alkyl- and arylplatinum complexes results in larger geometric deviations than with the corresponding simple alkyl- and arylplatinum complexes, PtMe$_3^+$ and PtPh$_3^+$, respectively. This suggests that higher levels of $\pi$-curvature and increased ability to favor delocalization of the electron density facilitate binding of Lewis bases to Lewis acidic Pt centers. However, a more subtle interplay between steric and electronic factors is obvious, since the same trends are not observed for the other Pt-doped buckybowl and fullerenes.

The trend of Lewis acidity suggested by chemical shift analysis is as follows [45]:

(5,0) Pt-doped SWCNT $\sim$ Pt-doped corannulene
$<$ Pt-doped C$_{24}$ IPP isomer $<$ Pt-doped C$_{24}$ HPP isomer $<$ Pt-doped sumane $<$ Pt-doped phenaline $<$ PtPh$_3^+$ $<$ PtMe$_3^+$,

which is virtually identical to the conclusion based on the adsorption of CO.

4.4. Lewis-Acid Catalyzed Diels-Alder Reaction between Maleic Anhydride and Cyclopentadiene. While CO coordination and maleic anhydride complexation provide ideas of Lewis acid strength of our organoplatinum complexes, perhaps the true test is their application as catalysts in a chemical reaction. The Diels-Alder reaction between maleic anhydride and cyclopentadiene is ideal for this purpose. This reaction is a [4+2] cycloaddition of a diene (i.e., cyclopentadiene) and an alkene (i.e., maleic anhydride) and generates a cyclohexene product. The key driving force is the formation of two new $\sigma$ bonds at the expense of two $\pi$ bonds. Lewis acids can promote this transformation by lowering the LUMO energy of the dienophile by binding to a Lewis basic site, leading to a more energetically favorable overlap between the dienophile LUMO and the diene HOMO (see Figure 26). This particular cycloaddition that we chose to study is also an example of what is termed a normal electron-demand Diels-Alder reaction. An inverse electron-demand Diels-Alder reaction involves molecular orbital interactions between the dienophile HOMO and the diene LUMO. In our studies, distortion of the electron density on the LUMO of the maleic anhydride was found to be typically quite small (Figure 30). In fact, significant interaction between the LUMO with the lobes on the model alkyl- and arylplatinum complexes could only be observed for Pt-doped corannulene. Decreased LUMO energies varied significantly for each of the model complexes investigated.

The cyclohexene product formed in the Diels-Alder reaction can exist as one of two diastereomeric compounds (Figure 26). The so-called endo-product is kinetically favored and involves secondary orbital interactions between the two unreactive C atoms on the diene and the $\pi$ orbitals of the neighboring C=O groups on the alkene [236]. In comparison, the exo-product is accessible through thermodynamic control. The distribution of isomeric products resulting from the Diels-Alder reaction depends on many parameters, including choice of the catalyst/ligand, solvent, and reaction temperature, among others.

Although PtMe$_3^+$ can be a catalyst for Diels-Alder reactions [237, 238], the use of Pt-doped supramolecules including buckybowl, fullerenes, and nanotubes has not yet been realized. Our investigations provide a preliminary insight into this possibility [45]. We considered exo- and endo-reaction pathways for our proposed catalysis and found similarity with previous studies of the Diels-Alder reaction, suggesting a concerted but asynchronous transition state [224–230, 239, 240]. In general, we can conclude that alkyl- and arylplatinum catalysts for the Diels-Alder reaction of maleic anhydride and cyclopentadiene results in an enhancement of reaction rate (Table 8). Interestingly, Pt-doped fullerene demonstrates only an approximate 3-fold rate increase, while systems displaying less ability to delocalize the electron density yield greater enhancements (up to 10$^7$-fold). Pt-doped SWCNT actually decreases the predicted reaction rate (i.e., it inhibits the reaction). Careful examination of the geometric structures revealed that ligands on Pt centers with extended $\pi$ frameworks typically give transition states that are more synchronous in character in comparison to the highly reactive and less sterically encumbered PtMe$_3^+$ and PtPh$_3^+$ (Figure 31). Thus, it seems that the polarization of the alkene and formation of the charged-separated species (see Figure 25) has the largest influence on catalyzing the [4+2] cycloaddition. The reason behind the enhanced reactivity, however, is not clear because the reaction we are studying involves two nonpolar starting materials (i.e., maleic anhydride and cyclopentadiene). Pyramidalization of the carbon framework, on the other hand, appears to have relatively little impact on the effectiveness of the proposed catalysis.

If we assume kinetic control of the Diels-Alder reaction, systems with higher levels of delocalization of the electron density in the catalyst tend to give lower preference for the endo-product. In fact, the catalyst that demonstrates the highest rate enhancements (i.e., PtMe$_3^+$) also exhibits the highest selectivity for the endo-product. Furthermore, in no cases is the exo-product favored over the endo-product. Based on these observations, it appears that decreased steric hindrance is ideal for promoting diastereoselectivity in the Diels-Alder reaction. The generality of this statement, however, requires further investigation since we have chosen a finite model of a SWCNT with H capping atoms to examine the feasibility of catalysis. Moreover, the interaction between two metal centers in close proximity of each other as substitutional dopant atoms in an extended carbon framework may play important roles in both the efficiency and selectivity in catalysis.

5. Proposed Applications of Substitutionally Doped SWCNTs

5.1. Substitutionally Doped SWCNTs in Nanosensors and Nanoelectronics. With the model SWCNTs and a brief examination of the interaction with gas molecules, we herein propose several applications of these macromolecules.
Table 6: Electronic structural data for alkyl- and arylplatinum complexes and their CO adsorbates [45].

<table>
<thead>
<tr>
<th>Pt complex</th>
<th>Σ^c</th>
<th>q(Pt)^h</th>
<th>E_{eic}^a</th>
<th>ΔG^b</th>
<th>d( Pt – C)</th>
<th>d( C=O)</th>
<th>ν_{C=O}^f</th>
<th>q( Pt/CO)^g</th>
<th>q( CO)^h</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtMe_3^+</td>
<td>297.5^c</td>
<td>0.77</td>
<td>–24.02</td>
<td>–8.25</td>
<td>2.116</td>
<td>1.156</td>
<td>2089.3</td>
<td>0.54</td>
<td>0.25</td>
</tr>
<tr>
<td>PtPh_3^+</td>
<td>315.4^c</td>
<td>0.77</td>
<td>–16.83</td>
<td>–0.46</td>
<td>2.113</td>
<td>1.160</td>
<td>2055.1</td>
<td>0.54</td>
<td>0.22</td>
</tr>
<tr>
<td>Pt-doped phenaline</td>
<td>279.6^c</td>
<td>0.74</td>
<td>–28.58</td>
<td>–13.07</td>
<td>2.057</td>
<td>1.161</td>
<td>2050.3</td>
<td>0.40</td>
<td>0.23</td>
</tr>
<tr>
<td>Pt-doped sumanene</td>
<td>260.5^c</td>
<td>0.77</td>
<td>–35.16</td>
<td>–19.67</td>
<td>2.025</td>
<td>1.163</td>
<td>2043.4</td>
<td>0.39</td>
<td>0.21</td>
</tr>
<tr>
<td>Pt-doped corannulene</td>
<td>257.8^c</td>
<td>0.59</td>
<td>–34.30</td>
<td>–18.22</td>
<td>1.983</td>
<td>1.179</td>
<td>1949.4</td>
<td>0.26</td>
<td>0.08</td>
</tr>
<tr>
<td>Pt-doped C_{24} fullerene PPP isomer</td>
<td>250.6^c</td>
<td>0.69</td>
<td>–31.58</td>
<td>–16.74</td>
<td>2.027</td>
<td>1.167</td>
<td>2017.3</td>
<td>0.32</td>
<td>0.17</td>
</tr>
<tr>
<td>Pt-doped C_{24} fullerene HPP isomer</td>
<td>268.3^c</td>
<td>0.66</td>
<td>–32.71</td>
<td>–17.59</td>
<td>1.995</td>
<td>1.166</td>
<td>2026.4</td>
<td>0.30</td>
<td>0.22</td>
</tr>
<tr>
<td>(5,0) Pt-doped SWCNT</td>
<td>292.2^c</td>
<td>0.53</td>
<td>–36.02</td>
<td>–20.31</td>
<td>1.971</td>
<td>1.179</td>
<td>1949.8</td>
<td>0.12</td>
<td>0.12</td>
</tr>
</tbody>
</table>

a Sum of angles around Pt center (without adsorbate).
b Partial charge on Pt atom (without adsorbate).
c Electronic energy of stabilization (in kcal/mol) upon CO adsorption.
d Free energy of stabilization (in kcal/mol) upon CO adsorption at 298 K.
e Bond length (in Å) between atoms X and Y.
f Vibration frequency (in cm^-1) of bound C=O molecule (cf. 2028.8 cm^-1 for unbound free CO).
g Partial charge of Pt atom in CO-adsorbed Pt complex.
h Partial charge on bound CO molecule.

Table 7: Electronic structural data for Lewis acid/maleic anhydride complexes [45].

<table>
<thead>
<tr>
<th>LA/MA complex</th>
<th>d(C1=O)</th>
<th>d(C1−C2)</th>
<th>d(C2=C3)</th>
<th>q(C1=O)</th>
<th>q(C2=C3)</th>
<th>δ(H)</th>
<th>Δδ(H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoordinated maleic anhydride</td>
<td>1.223</td>
<td>1.499</td>
<td>1.351</td>
<td>–0.496</td>
<td>–0.250</td>
<td>6.25</td>
<td>0.00</td>
</tr>
<tr>
<td>PtMe_3^+ /MA</td>
<td>1.248</td>
<td>1.488</td>
<td>1.354</td>
<td>–0.583</td>
<td>–0.215</td>
<td>7.02</td>
<td>0.77</td>
</tr>
<tr>
<td>PtPh_3^+ /MA</td>
<td>1.243</td>
<td>1.488</td>
<td>1.354</td>
<td>–0.557</td>
<td>–0.221</td>
<td>6.94</td>
<td>0.69</td>
</tr>
<tr>
<td>Pt-doped phenaline/MA</td>
<td>1.249</td>
<td>1.486</td>
<td>1.356</td>
<td>–0.584</td>
<td>–0.229</td>
<td>6.80</td>
<td>0.55</td>
</tr>
<tr>
<td>Pt-doped sumanene/MA</td>
<td>1.249</td>
<td>1.484</td>
<td>1.356</td>
<td>–0.577</td>
<td>–0.221</td>
<td>6.71</td>
<td>0.46</td>
</tr>
<tr>
<td>Pt-doped corannulene/MA</td>
<td>1.278</td>
<td>1.440</td>
<td>1.384</td>
<td>–0.643</td>
<td>–0.311</td>
<td>5.53</td>
<td>–0.72</td>
</tr>
<tr>
<td>Pt-doped C_{24} fullerene PPP isomer/MA</td>
<td>1.254</td>
<td>1.472</td>
<td>1.363</td>
<td>–0.595</td>
<td>–0.266</td>
<td>6.30</td>
<td>0.05</td>
</tr>
<tr>
<td>Pt-doped C_{24} fullerene HPP isomer/MA</td>
<td>1.245</td>
<td>1.479</td>
<td>1.359</td>
<td>–0.552</td>
<td>–0.250</td>
<td>6.39</td>
<td>0.14</td>
</tr>
<tr>
<td>(5,0) Pt-doped SWCNT/MA</td>
<td>1.265</td>
<td>1.451</td>
<td>1.376</td>
<td>–0.604</td>
<td>–0.297</td>
<td>5.63</td>
<td>–0.62</td>
</tr>
<tr>
<td>AlMe_3/MA</td>
<td>1.238</td>
<td>1.487</td>
<td>1.355</td>
<td>–0.597</td>
<td>–0.245</td>
<td>6.36</td>
<td>0.11</td>
</tr>
<tr>
<td>AlCl_3/MA</td>
<td>1.245</td>
<td>1.490</td>
<td>1.353</td>
<td>–0.675</td>
<td>–0.225</td>
<td>6.60</td>
<td>0.35</td>
</tr>
<tr>
<td>BF_3/MA</td>
<td>1.244</td>
<td>1.492</td>
<td>1.352</td>
<td>–0.561</td>
<td>–0.234</td>
<td>6.48</td>
<td>0.23</td>
</tr>
<tr>
<td>SnCl_4/MA</td>
<td>1.241</td>
<td>1.492</td>
<td>1.352</td>
<td>–0.622</td>
<td>–0.233</td>
<td>6.46</td>
<td>0.20</td>
</tr>
<tr>
<td>TiCl_4/MA</td>
<td>1.237</td>
<td>1.492</td>
<td>1.352</td>
<td>–0.508</td>
<td>–0.236</td>
<td>6.41</td>
<td>0.16</td>
</tr>
</tbody>
</table>

a Bond length (in Å) between atoms X and Y.
b Partial charge on O atom.
c Partial charge on C3 atom.
d Chemical shift (in ppm) on H atom (referenced to tetramethylsilane).
e Difference in chemical shift (in ppm) on H atom relative to uncoordinated maleic anhydride (referenced to tetramethylsilane).

Since defected SWCNTs can react with dissolved NO to form N-doped SWCNTs [81], it is possible that injecting such nanostructures into biological systems may provide promise for use as an artificial antioxidant. However, because of the huge thermodynamic preference for chemical reactions between 5-1DB defects and NO, reversibility of this process comes into question. Nonetheless, we know that introduction of N atoms results in increased clearance rates [123] and, hence, may provide a strategy for removing these macromolecules after they have undergone irreversible NO capture. We can imagine a scenario in which vacancy defects are formed via high-energy processes [83, 84], such as the harmful UV-A and UV-B rays from the sun. If pristine SWCNTs can be implanted into the human body, environmental stresses may trigger the formation of 5-1DB defects and provide a queue to decrease the amount of free biological NO in the body and thereby maintain homeostasis.

Another possible use of defected SWCNTs would be as a sensor for biological NO [241]. Perhaps a more intriguing starting point for the development of a nanosensor, however, would be our proposed transition metal-doped SWCNTs [113]. We feel that Pt-doped SWCNTs are of specific interest due to their ability to adsorb a wide array of small gaseous molecules. The key strategy for analyzing and detecting...
adsorption would be in monitoring the electronic structure of HSWCNTs. Thus, our proposal below also pertains to the possibility of using Pt-doped SWCNTs in nanoelectronics.

In theory, minor fluctuations in electronic structure can be evaluated by considering the amount of charge transfer that takes place between the nanotube superstructure and the small molecule adsorbate. Additionally, analysis of the HOMO–LUMO gap may provide some insight. Peng and coworkers have previously suggested that charge transfer between the nanotube and adsorbate can result in a change in the conductance along the axis as described by the following relationship [71]:

\[ \Delta Q = C_g \cdot \Delta V_g = \delta \frac{\pi dl}{\sigma}, \]  

where \( \Delta Q \) is the charge transfer, which is directly proportional to the capacitance, \( C_g \), and the observed voltage change, \( \Delta V_g \). The nanotube length and diameter are \( l \) and \( d \), respectively, while \( \sigma \) and \( \delta \) are the molecular cross-section area and coverage, respectively [71]. From Table 9, the trend between the adsorbate species and net charge transfer is clear.

In our investigations [113], although the magnitude of charge transfer is small, it has been demonstrated that a value of 0.28 is sufficient for observing macromolecular changes in measurable quantities such as conductivity (in the case of B- and N-doped SWCNTs), hence ratifying their application as nanosensors. It is also possible that extension of these terminated fragments in either direction ad infinitum with multiple doping sites per nm of nanotube should enhance the sensitivity enough such that a practically useful device can be prepared based on these macromolecules. Additionally, other strategies, including the use of a polymer matrix to encapsulate these structures, may also help. For instance, carbon nanotubes have demonstrated that their inclusion in insulating polymer matrices can cause the resulting material to become conductive above a certain filler concentration known as the percolation threshold [34]. Bryning et al. have demonstrated that this value can be as low as 0.005 vol% in SWCNT/epoxy composites [242].

Furthermore, one can also envision the utilization of these macromolecules as nanowires [33]. In nanoelectronics, carbon nanotubes have been proposed as field effect transistors (FETs) [11, 12, 15, 243], optoelectronic devices, and nanoelectromechanical systems (NEMS) [244, 245]. In fact, carbon nanotubes have been used to build an FET with a back gate (e.g., Infineon Technologies). In this design, the carbon nanotube is situated at the top of electrodes, which themselves are separated by a dielectric spacer to the backgate. The conductive nanochannel hence provides a connection between the drain and source electrodes. Applications of devices of this type, such as in non-volatile molecular memory elements, have been considered [14, 246]. As such, the ability of manipulating conductance across a wire with simple exposure to gases would be an attractive one since this would provide a relatively straightforward method for controlling a nanocircuit. In theory, should the conductance of the carbon nanotube be too high, introduction of a gaseous atmosphere of CO, for instance, should increase resistivity. This effect would be compounded if a single SWCNT was doped at multiple sites. The key advantage to electronic manipulation of this type is the ability to reversibly control conductivity by removal of the resistive gas by purging the atmosphere with inert gases such as argon. Because of the high diffusion rates of gaseous molecules, extremely fast circuit breaks are possible. In the future, more complicated electronic devices may contain differentially doped SWCNT that may be selectively modified in terms of its electronic structure depending on the nature of the adsorbate. Obviously, selective modification of one SWCNT in the presence of thousands of others remains a significant challenge and may require new engineering solutions.

### 5.2. Substitutionally Doped SWCNTs in Nanocatalysis

Based on our studies, the additional \( \pi \)-delocalization of electrons in Pt-doped supramolecular frameworks (e.g., buckybowls, fullerenes, and nanotubes) appears to offer less useful rate enhancements and selectivities in comparison with the readily available simple PtMe₃⁺ system [45]. Again, we believe that using Pt-doped SWCNTs and other transition metal-doped congeners as catalysts warrant further investigation. Since these nanomaterials sit at the boundary between homogeneous and heterogeneous catalysis, their independent synthesis and characterization may provide an opportunity to establish the connection between reaction mechanisms of these two types of catalysis. Additionally, we may also view substitutional doping with Pt atoms as a strategy for developing heterogeneous Lewis acid catalysis, in which immobilization of reactive Lewis acids may allow for recovery and reuse of precious metals.

We also envision that more complex systems may be possible in the case of substitutional doping. In fact, because nanotubes are channels, we may one day be able to achieve a nanoscale version of microfluidics. For instance, we can imagine a SWCNT with a smaller diameter with substitutional transition metal doping that can act as catalysts that are themselves encased in a SWCNT with a much larger diameter. These nanochannels may provide enhanced chemical reactivity due to higher local concentrations of the reactive partners. We can even dream of synthesizing nanotubes containing multiple substitutional dopants of either the same or different transition metal in which their proximity provide unique types of catalysis that are not possible in the homogeneous bulk solution. Nanocatalysis remains an emerging field that will continue to develop in the years to come.

### 6. Concluding Remarks

Within DFT, the rich chemistry of substitutionally doped SWCNTs has been investigated. We summarize our findings as follows:

1. A vacancy defect formed by removal of a single C atom from the sidewall of a SWCNT can undergo structural rearrangement to give a structure containing a five-membered carbocycle and a single C atom with one dangling bond (i.e., the 5-1DB defect).
Table 8: Free energies and rates of the Diels-Alder reaction of maleic anhydride and cyclopentadiene as catalyzed by alkyl- and arylplatinum complexes [45].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\Delta G_{\text{exo}}^a$</th>
<th>$\Delta G_{\text{exo}}^b$</th>
<th>$\Delta G_{\text{endo}}^c$</th>
<th>$\Delta G_{\text{exo}}^d$</th>
<th>$\Delta G_{\text{endo}}^e$</th>
<th>$k_{\text{endo}}/k_{\text{exo}}^f$</th>
<th>$k_{\text{cat}}/k_{\text{uncat}}^g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>27.28</td>
<td>-3.83</td>
<td>26.67</td>
<td>-3.03</td>
<td>0.60</td>
<td>2.78</td>
<td>1.00</td>
</tr>
<tr>
<td>PtMe$_3^+$</td>
<td>15.85</td>
<td>-8.06</td>
<td>14.41</td>
<td>-9.54</td>
<td>1.44</td>
<td>11.43</td>
<td>$1.27 \times 10^5$</td>
</tr>
<tr>
<td>PtPh$_3^+$</td>
<td>17.43</td>
<td>-8.19</td>
<td>16.82</td>
<td>-8.48</td>
<td>0.61</td>
<td>2.79</td>
<td>$1.58 \times 10^5$</td>
</tr>
<tr>
<td>Pt-doped phenaline</td>
<td>17.69</td>
<td>-8.15</td>
<td>16.76</td>
<td>-7.70</td>
<td>1.02</td>
<td>5.60</td>
<td>$1.47 \times 10^5$</td>
</tr>
<tr>
<td>Pt-doped sumanene</td>
<td>16.76</td>
<td>-8.57</td>
<td>16.19</td>
<td>-8.40</td>
<td>0.57</td>
<td>2.63</td>
<td>$3.01 \times 10^5$</td>
</tr>
<tr>
<td>Pt-doped corannulene</td>
<td>16.03</td>
<td>-13.26</td>
<td>15.30</td>
<td>-13.28</td>
<td>0.73</td>
<td>3.43</td>
<td>$8.22 \times 10^5$</td>
</tr>
<tr>
<td>Pt-doped C$_{24}$ PPP isomer</td>
<td>23.54</td>
<td>-4.04</td>
<td>22.68</td>
<td>-3.45</td>
<td>0.86</td>
<td>4.26</td>
<td>1.42</td>
</tr>
<tr>
<td>Pt-doped C$_{24}$ HPP isomer</td>
<td>23.49</td>
<td>-4.47</td>
<td>22.49</td>
<td>-4.17</td>
<td>1.00</td>
<td>5.44</td>
<td>2.99</td>
</tr>
<tr>
<td>(5,0) Pt-doped SWCNT</td>
<td>30.23</td>
<td>2.47</td>
<td>30.11</td>
<td>-3.47</td>
<td>0.12</td>
<td>1.23</td>
<td>0.55</td>
</tr>
</tbody>
</table>

\(^a\) Free energy (in kcal/mol) required to reach transition state leading to exo-product at 298 K.

\(^b\) Free energy (in kcal/mol) change to exo-product in at 298 K.

\(^c\) Free energy (in kcal/mol) required to reach transition state leading to endo-product at 298 K.

\(^d\) Free energy (in kcal/mol) change to endo-product at 298 K.

\(^e\) Difference in free energy (in kcal/mol) changes required to reach transition states leading to endo- and exo-products at 298 K.

\(^f\) Relative rate leading to endo-product versus exo-product.

\(^g\) Relative rate of catalyzed Diels-Alder reaction versus uncatalyzed Diels-Alder reaction.

Table 9: Charge transfer and HOMO–LUMO gap data for nanotube-adsorbate complexes with side-on binding motif [113, 114].

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Average charge transfer (^a)</th>
<th>HOMO–LUMO gap (eV)</th>
<th>Change in HOMO–LUMO gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>N/A</td>
<td>0.74</td>
<td>0</td>
</tr>
<tr>
<td>CO(^b)</td>
<td>0.05</td>
<td>0.78</td>
<td>0.04</td>
</tr>
<tr>
<td>NO(^c)</td>
<td>0.28</td>
<td>0.74</td>
<td>0.00</td>
</tr>
<tr>
<td>NH$_3^d$</td>
<td>-0.18</td>
<td>0.75</td>
<td>0.01</td>
</tr>
<tr>
<td>N$_2^e$</td>
<td>0.09</td>
<td>0.81</td>
<td>0.07</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.34</td>
<td>0.70</td>
<td>-0.04</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>0.25</td>
<td>0.88</td>
<td>0.14</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>0.38</td>
<td>0.88</td>
<td>0.14</td>
</tr>
</tbody>
</table>

\(^a\) Represents charge donated from the Pt-doped SWCNT to the adsorbate.

\(^b\) Represents ($\text{CO})_2$-adsorbed HSWCNT.

\(^c\) Represents ($\text{NO})_2$-adsorbed HSWCNT.

\(^d\) Represents ($\text{NH}_3)_2$-adsorbed HSWCNT.

\(^e\) Represents ($\text{N}_2)_2$-adsorbed HSWCNT.

This active vacancy reacts with NO liberating NO$_2$ and N-doped SWCNTs in a selective fashion.

(2) 5-1DB defects can react with O$_3$ to generate O$_2$ and O-doped SWCNTs in a selective fashion. Substitutional O-doping yields a structure containing a C–O bond exhibiting strong similarities to C=O double bonds.

(3) Substitutional doping with transition metals, such as Pt, results in slight buckling of the nanotube sidewall to give a structure in which the transition metal dopant is situated in a position protruding to the exterior of the sidewall and the Pt atom and three adjacent C atoms are situated in a tripodal fashion.

(4) Substitutional doping with transition metals depends strongly on the doping location. Nanotubes capped with fullerene hemispheres can be doped either at the cap or the sidewall. Cap doping gives chemical reactivities more similar to the corresponding transition metal-doped fullerenes. Sidewall doping offers different opportunities for chemical reactions.

(5) Adsorption of small molecules onto Pt-doped SWCNTs is analogous to coordination chemistry of alkylplatinum complexes with one caveat. Namely, because the nanotube provides much larger steric bulk, multiple adsorption may become thermodynamically unfavorable. However, weak interaction with the extended delocalized $\pi$-electrons may play a role.

(6) Adsorption provides a facile method for manipulating electronic structure of Pt-doped SWCNTs. This is because coordination of adsorbates to the Pt atom embedded in the sidewall of SWCNTs can result in either ligand-to-metal or metal-to-ligand charge transfer, depending on the nature of the adsorbate. This results in manipulation of the HOMO–LUMO gap.
(7) Pt-doped SWCNTs exhibit Lewis acidity similar to that of simple alkyl- and arylplatinum complexes. Evaluation of Lewis acid strength can be done by measuring the stretching frequency of a bound molecule of CO or by 1H NMR studies of the β-H of Lewis acid/Lewis base complexes formed with α,β-unsaturated carbonyl compounds. However, because the nanotube provides larger steric bulk than simple alkyl- and arylplatinum complexes, the ability to activate a substrate for catalysis may be impeded.

Without doubt, since transition metal-doped SWCNTs have yet to be prepared experimentally, much of the work presented here remains a theoretical prediction. Nonetheless, we have provided a comprehensive overview of the potential of these materials. Their behavior in polymer composites, in particular, may provide a handle by which some of these properties can be amplified to useful levels. Further research involving computational studies using periodic boundary conditions as well as experimental efforts will provide a closer look at potential of these nanomaterials as nanosensors, nanocatalysts, and nanodevices. Our initial investigations here will provide inspiration and guidance to experimentalists in their endeavors.

Acknowledgments

The authors thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support. WestGrid and C-HORSE have provided the necessary computational resources. C. S. Yeung gratefully acknowledges NSERC for an Undergraduate Student Research Award.

References


