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Organometallic chemistry of graphene: Photochemical complexation of graphene with group 6 transition metals

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A B S T R A C T

We report the experimental realization of η^6-complexes of group 6 transition metals with a single layer graphene using photo-activated reactions with organometallic compounds. The reaction progress was followed by in-situ measurements of the graphene conductivity. We observed that the chromium reagents exert the strongest effect on the electronic properties of graphene, leading to (η^6-graphene)CrL [$L = C_6H_6$, $(CO)_3$] complexes with enhanced conductivity. Thus, in the case of covalent functionalization of graphene with $Cr(CO)_6$, the conductivity increased by a factor of 4, while the (η^6- C_6H_6)$Cr(CO)_3$ reagent doubled the conductivity producing the least enhancement. This mode of covalent bonding preserves the conjugation and the planarity of the graphene structure and offers a promising route for the preparation of a new class of graphitic materials functionalized with transition metals, which may find applications in optoelectronics, spintronics and magnetic nanodevices.

1. Introduction

Carbon allotropes are envisioned as versatile building blocks of next generation electronics. In particular graphene and graphene-like structures have been the subject of intense research in the past decade due to their excellent electronic, optical, thermal and mechanical properties [1,2]. Major challenges associated with the utilization of graphene in electronics are the formation of ohmic contacts and band-gap engineering. The organometallic chemistry that utilizes transition metal atoms bound to extended, periodic π-electron carbon systems can provide a solution to both of these issues. Hexahapto coordination of transition metals to the benzenoid ring of graphene surfaces was demonstrated to seamlessly interconnect single-walled carbon nanotubes (SWNTs) and graphene layers [3–8]. Apart from serving as a conduit for electron transport between conjugated carbon surfaces, the η^6-bond of chromium to a single layer graphene has shown promise in the preparation of high mobility devices [9].

A number of high level calculations have confirmed the viability of the hexahapto organometallic bond to the benzenoid rings in carbon nanotubes and graphene [10–14]. Furthermore, sophisticated first principle calculations predict the formation of stable periodic graphene/Cr/ligand structures with ferromagnetic ordering at the ground electronic state [11], which suggests that synthesis of ordered transition metal – graphene structures may find applications in spintronics and quantum computing.

The potential of the organometallic approach to the functionalization of conjugated carbon allotropes is exemplified in the classic model compound from organic chemistry – bis(benzene) chromium, in which the metal atom coordinates to two benzene ligands. The complex is stable due to the formation of a full 18-electron valence shell in which the metal and the two benzene ligands each donate 6 e^-. The metal exists in zero oxidation state and due to the large degree of delocalization of the electrons from the central metal atom into the ligand, these compounds are highly covalent. Despite the formation of a covalent bond, the ligands (benzene, graphene) retain their planarity, which together with the preserved electron delocalization is essential for the electronic properties of π-electron systems. Thus, this mode of functionalization is expected to provide graphene structures that possess high carrier mobility.

It is important to refer to the theoretical assessment of the planarity of conjugated carbon system in order to understand the

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effect that it exerts on the electronic structure and properties of the system. The degree of nonplanarity in π-electron systems can be quantitatively expressed by the pyramidalization angle [θ_P] [15,16], which is 0° for sp^2 hybridized carbon atoms and 19.5° for sp^3 hybridized carbon atoms (Fig. 1). In bis(benzene) chromium the pyramidalization angle of the carbon atoms is $\theta_P = 1.7°$, and with an increase of the number of benzene rings in the structure, as is the case of a graphene lattice, the degree of pyramidalization is expected to decrease due to the rigidity of the network of benzene rings. Thus, θ_P was found to be less than 0.2° in the $C_{96}H_{24}{-}Cr(CO)_3$ graphene fragment (Fig. 1c), indicating preserved planarity of the graphene sheet upon functionalization with chromium atoms [14,17]. Importantly, the pyramidalization angle has a defined relationship with the change in electronic structure that occurs during pyramidalization of a carbon atom as illustrated in Fig. 1a [15]. It is apparent from the plot that at such small pyramidalization angle, the sp^2 character of the carbon atoms that participate in the hexahapto bond formation, is essentially preserved and this type of covalent functionalization is classified as *constructive rehybridization* [18].

Furthermore, graphene is considered an ideal ligand for hexahapto complexation [4] because the valence and conduction bands touch at the Dirac point, and both the degenerate bonding (e_{1g}) and anti-bonding (e_{2u}) benzene π-orbitals are readily available for hybridization with the transition metal d-orbitals [4].

While extending the hexahapto coordination of transition metals to graphene, which is essentially an extended polyaromatic hydrocarbon, may seem to be a logical step, the experimental realization of these structures is not trivial. The initial experimental studies have made use of conventional organometallic techniques such as metal vapor synthesis (e-beam) and thermal solution chemistry to form hexahapto bonds between transition metal atoms and conjugated carbon surfaces [3,18].

Here we investigate the interaction of the group 6 transition metals with the surface of a single layer graphene and report the formation of graphene-transition metal mono-hexahapto complexes that exhibit enhanced electrical conductivity. For these experiments we utilize chemical vapor deposition (CVD) graphene, which is transferred on a glass substrate with pre-patterned gold electrodes. The graphene was reacted with different organometallic reagents using a photochemical route [19] and the reaction progress was followed by *in-situ* measurements of the graphene conductivity.

2. Methods

2.1. Preparation of graphene devices

As-grown single layer CVD graphene (Graphene Supermarket, USA) was transferred to a glass substrate with pre-patterned gold contacts (10 nm Cr/100 nm Au) using a cellulose-assisted transfer (CAT) method [20]. Briefly, CVD graphene on copper was spin-coated with cellulose acetate dissolved in acetone, followed by dissolving the Cu foil in an H_2O_2/HCl etching solution. The transferred graphene was washed thoroughly with acetone to remove the cellulose acetate. Typical film dimensions were 2 mm (width) and 4 mm (length). The samples were annealed in vacuum (10^{-7}-10^{-8} torr) at 200 °C for 2 h inside a glass tube and immediately transferred into a glovebox for conducting the photochemical reactions.

2.2. Photochemical reactions

Solutions of $Cr(CO)_6$, $Mo(CO)_6$ (Sigma Aldrich 98%), $W(CO)_6$ (Alfa Aesar 97%), $Cr(\eta^6\text{-benzene})(CO)_3$ and $Cr(\eta^6\text{-benzene})_2$ were prepared in degassed acetonitrile inside a glovebox at a concentration of 1×10^{-3} M. A drop (~0.1 mL) of the transition metal reagent solution was cast onto the graphene surface inside the glovebox, followed by irridation with a light source: UVC [254 nm] was employed for $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, UVA [365 nm] – in the case of $Cr(\eta^6\text{-benzene})(CO)_3$, and room light for $Cr(\eta^6\text{-benzene})_2$.

2.3. Characterization

The resistance was recorded with a Keithley 236 source measure unit controlled with a Labview program. The temperature

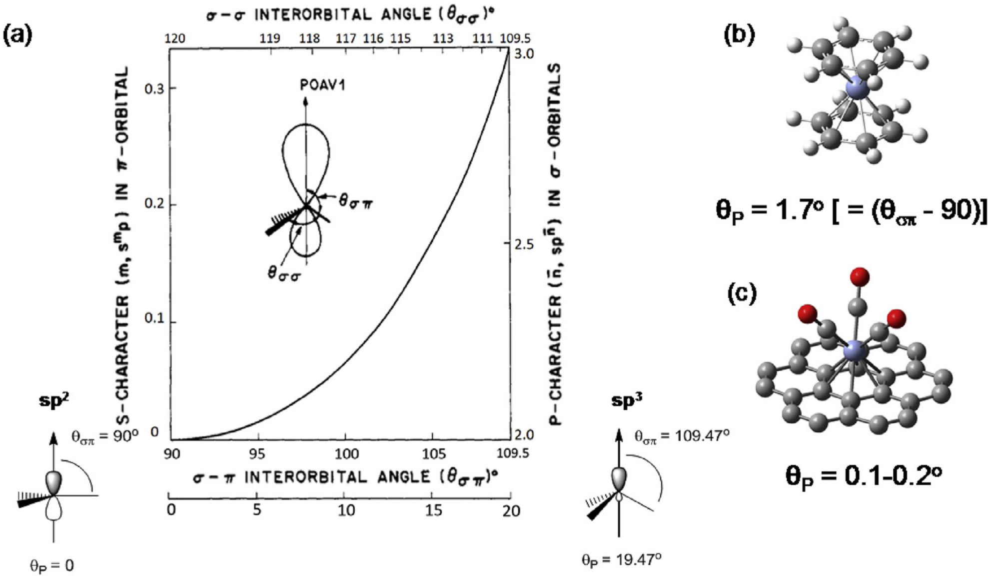

Fig. 1. (a) Relationship between the σ–σ and σ–π interorbital angles and the hybridization at a carbon atom between the extremes of sp^2 (planar geometry) and sp^3 hybridization (tetrahedral geometry) in C_{3v} symmetry. Reprinted with permission from Ref. [15] Copyright 1988 American Chemical Society. (b) structure of bisbenzene chromium with the pyramidalization angle $\theta_P = 1.7°$ (c) sub-unit of a $C_{96}H_{24}{-}Cr(CO)_3$ graphene fragment illustrating θ_P of the coordinated carbon atoms ~ 0.1–0.2°. (A colour version of this figure can be viewed online.)

dependence of resistance was measured with a Quantum Design cryogenic physical property measurement system (see Supporting Information, Fig. S3c).

UV–vis spectra of solutions of the transitional metal reagents in acetonitrile and graphene films transferred on quartz were obtained with a Varian Cary 5000 spectrophotometer. Raman spectra and maps were collected with a Nicolet Almega XR Dispersive Raman microscope with a 0.7 μm spot size and 532 nm laser excitation.

3. Results and discussion

Transition metal organometallic complexes, in particular metal carbonyls, are extremely photosensitive [21] and we have previously shown that this provides a mild reaction route to interconnect the conjugated surfaces of carbon nanotubes in thin film networks [19]. This has led to materials with increased dimensionality and enhanced conductivity. Here we investigate the effect of transition metal hexahapto functionalization on the electrical conductivity of a single graphene layer utilizing the photochemical route for functionalization. The current reaction set up will lead to the formation of half-sandwich graphene structures in contrast to the previously prepared atomically connected graphene surfaces [8].

For this study large-area single-layer graphene films (CVD grown) were transferred on a glass substrate with pre-patterned gold contacts. After thorough washing, the graphene films were annealed to prepare clean pristine graphene devices. The quality of the graphene films was assessed with SEM and Raman spectroscopy. SEM and optical images of a representative transferred graphene film are shown in Fig. 2a and Fig. 2b, respectively. A typical Raman spectrum in Fig. 2c shows the characteristic G- and 2D bands with a high intensity ratio of >2; a small D-peak was observed in some areas of the graphene film as visualized in the Raman D-peak map depicted in Fig. 2d. The Raman spectroscopy and measurements of FET devices annealed at mild conditions (200 °C for 2 h in vacuum, see experimental section and reference [20]) confirmed that this transfer technique provides clean graphene films without contaminations from a polymer carrier, which is crucial for study of the graphene chemistry.

Immediately following annealing, the graphene films were transferred into a glove box without exposure to air and electrically connected to Keithley 236 measure unit through feedthroughs on the back of the glove box. The reactions of graphene films with the chromium reagents were performed by placing a drop of a reagent solution on the graphene surface, followed by exposure to UV light. The light source for the photochemical reactions were selected based on the absorption spectra of the reagents: Cr(CO)$_6$, Mo(CO)$_6$ and W(CO)$_6$ [19], shown in Fig. 3a; the wavelength of the light used to initiate the reaction is indicated with a dash line. We begun the study with employing metal (M=Cr, Mo, W) hexacarbonyl reagents dissolved in acetonitrile. The UV–vis spectra of all tree reagents are similar; they exhibit two intense bands at ~230 nm and 285 nm, both associated with the $M \rightarrow \pi^*$ CO charge transfer (CT) absorption. The ligand field absorption, typically observed at ~330 nm appears as a shoulder to the 285 nm peak, and it is not very pronounced in our measurements. We utilized UVC light (254 nm) for the photochemical reaction of M(CO)$_6$ with graphene; the electronic transition excited at this wavelength is predominantly the metal to ligand ($M \rightarrow \pi^*$CO) transition. The 254 nm photons have an energy of ~113 kcal/mol, while the Cr–CO bond dissociation is about 37 kcal/mol [22,23].

As can be seen in Fig. 3c, irradiation of the graphene film exposed to a solution of Cr(CO)$_6$ in acetonitrile, leads to an increase of the conductivity, which doubles in 25 s and saturates in less than 3 min (after ~160 s) to give a conductivity enhancement by a factor of 4. Irradiation of graphene in the solvent (acetonitrile) nearly had no effect on the graphene conductivity (Fig. 3c, blank). Thus, we suggest that graphene reacts with the photoactivated Cr(CO)$_6$ to yield a hexahapto complex following the mechanism illustrated in Fig. 3d. It is known that the photolysis of metal carbonyls in solution proceeds through cleavage of a single metal-CO bond and the formation of coordinatively unsaturated metal carbonyls M(CO)$_5$, which are highly reactive species and rapidly bind solvents [24]. It

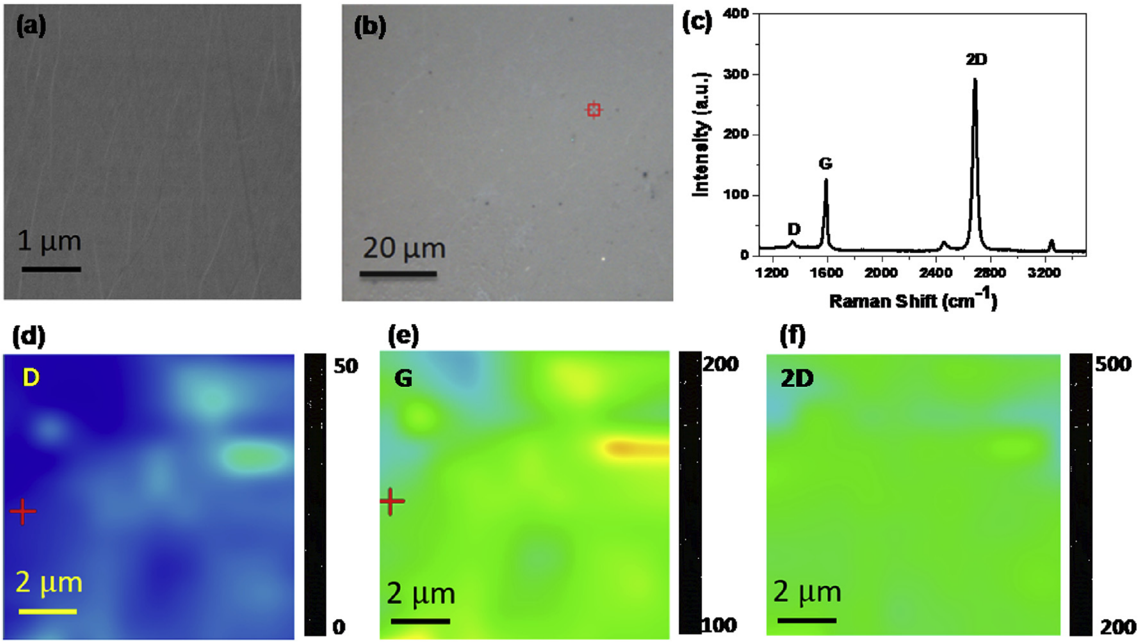

Fig. 2. CVD graphene transferred on a glass substrate. (a) SEM image (b) optical image and (c) Raman spectrum of a transferred graphene film. (d–f) Maps of the Raman intensity of the D-, G- and 2D-peaks of the transferred graphene film, respectively. (A colour version of this figure can be viewed online.)

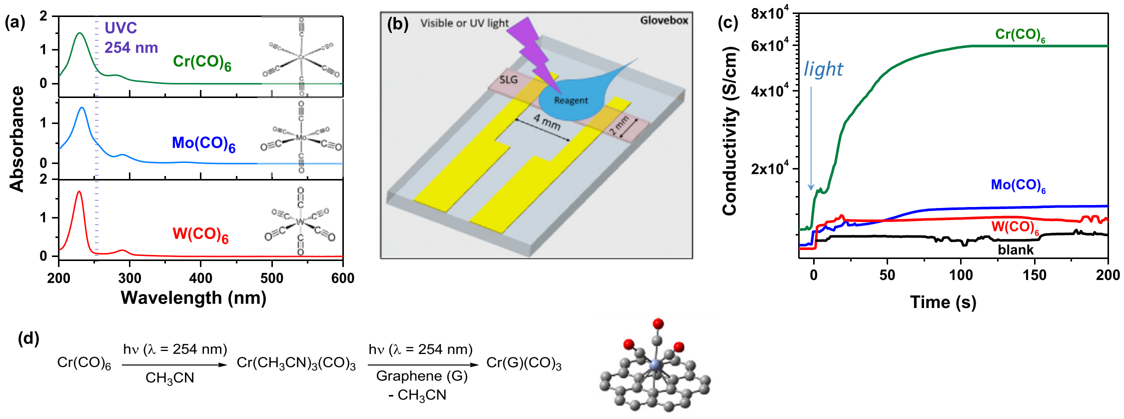

Fig. 3. Photochemical reaction of graphene with $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$. (a) UV–vis spectra of the hexacarbonyl reagents in acetonitrile (b) Schematic illustration of the experimental set-up (c) Evolution of graphene conductivity upon photochemical reaction with the hexacarbonyl reagents; the black line (blank) shows the preserved graphene conductivity during irradiation of the film exposed to the solvent – acetonitrile. (d) Reaction mechanism of graphene with $Cr(CO)_6$ upon illumination with 254 nm. (A colour version of this figure can be viewed online.)

is reasonable to postulate that CH_3CN in $Cr(CO)_3(CH_3CN)_3$ was replaced readily by graphene to form $Cr(\eta^6\text{-graphene})(CO)_3$, which preserves the delocalized band structure of graphene due to the constructive rehybridization of the graphene π-system with the vacant chromium d_π orbital. The irradiation of a graphene device in presence of an acetonitrile solutions of $Mo(CO)_6$ and $W(CO)_6$ does not lead to much enhancement of the device conductivity ($\sigma-\sigma_o/\sigma_o \sim 0.5$, Fig. 3c), suggesting that the photoreaction proceeds with a limited yield. This may be due to the very low quantum efficiency of production of substituted products, such as $M(CO)_4L_2$, where L = acetonitrile [25].

We further explored the effect of the photochemical reaction of graphene with $Cr(\eta^6\text{-benzene})(CO)_3$ and $Cr(\eta^6\text{-benzene})_2$ on the conductivity of the graphene films. The reactions were conducted at 365 nm in the case of $Cr(\eta^6\text{-benzene})(CO)_3$ and visible light when $Cr(\eta^6\text{-benzene})_2$ was employed (Fig. 4a). In both cases an abrupt increase of conductivity was recorded as illustrated in Fig. 4b. The reaction with bi(sbenzene) chromium leads to an increase of conductivity by a factor of ~3.5 and the maximum increase is reached within 10 s, indicating that the ligand exchange proceeds much faster than in the case of $Cr(CO)_6$.

The conductivity measurements indicate that the reactivity of the $Cr(\eta^6\text{-benzene})(CO)_3$ reagent presents a case that is between $Cr(CO)_6$ and $Cr(\eta^6\text{-benzene})_2$, in the sense that there is an initial abrupt increase of conductivity (within the first 10 s), which is then followed by a gradual conductivity increase and saturation after 110 s. The observed two-fold enhancement of conductivity is the lowest among all three chromium reagents (Fig. 4c).

Comparing the reaction kinetics and the degree of conductivity enhancement produced by the reactions we conclude that the ligand exchange occurs much faster when the graphene substitutes benzene rather than CO.

The proposed mechanisms of photochemical reactions of $Cr(\eta^6\text{-benzene})_2$ and $Cr(\eta^6\text{-benzene})(CO)_3$ with graphene are shown in Fig. 4d. The photochemistry of $Cr(\eta^6\text{-benzene})(CO)_3$ is complicated, as both arene exchange and CO loss can occur during exposure to UV light, however the exchange of the two-electron donor ligand (CO) is more common as compared to the six electron benzene

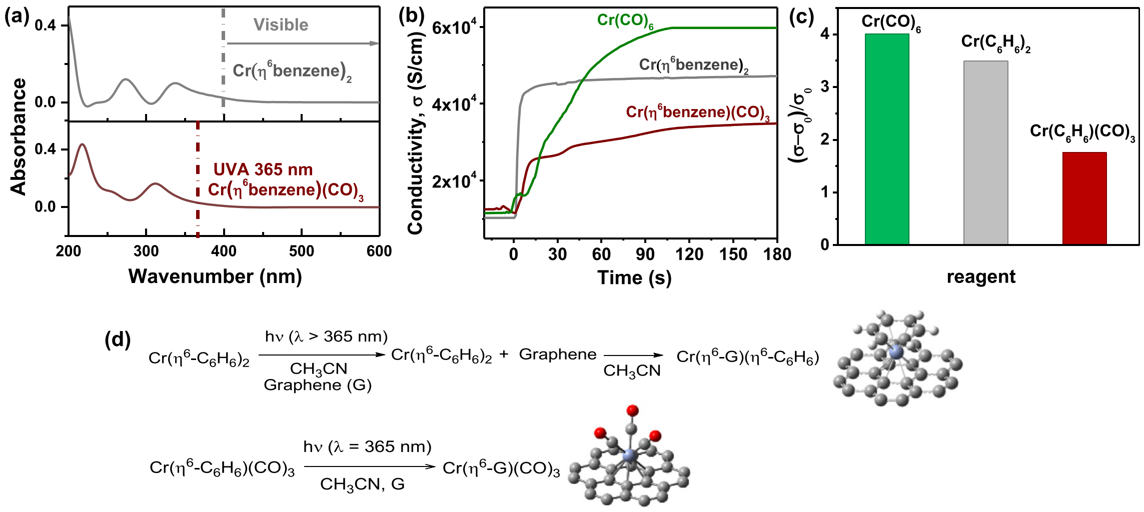

Fig. 4. (a) Absorption spectra of $Cr(\eta^6\text{-benzene})(CO)_3$ and $Cr(\eta^6\text{-benzene})_2$ in acetonitrile (b) Evolution of conductivity of graphene films on photochemical reaction with the chromium reagents. (c) Conductivity enhancement of graphene half sandwich complexes formed with three different chromium reagents. (d) Schematic illustration of the mechanism of the photochemical reactions of graphene with $Cr(\eta^6\text{-benzene})(CO)_3$ and $Cr(\eta^6\text{-benzene})_2$. (A colour version of this figure can be viewed online.)

ligand exchange [21]. Thus, the photochemical reaction with graphene most likely proceeds through a loss of CO from the Cr(η^6-benzene)$(CO)_3$ reagent and formation of the (η^6-benzene)Cr(η^6-graphene) complex (Fig. 4d).

It has been argued that the primary means of conductivity modulation in graphene devices is the alteration of barrier heights at contacts. To eliminate the effect of contacts on the conductivity of graphene in our experiments we performed similar tests with adding a small drop of an acetonitrile solution of $Cr(CO)_6$ to the middle section of the graphene film, away from the metal contacts. These experiments confirmed that the conductivity increase of the graphene films is not due to contact effects (see Supporting Information Fig. S1). Thus, we conclude that the observed conductivity enhancement in mono-hexahapto transition metal - functionalized graphene is due to the formation of new bonds between the metal atoms and the bezenoid rings of the graphene lattice. The presence of Cr on the graphene surface was confirmed by XPS analysis (see Supporting Information, Fig. S2). Further characterization, including Raman, absorption spectroscopy and temperature dependence of resistance (Supporting Information, Fig. S3) did not show evidence for doping (charge transfer), however it should be noted that these measurements were done on samples exposed to air. The compounds reported here are air sensitive and future characterization would require encapsulation of the functionalized device structures.

The interaction between graphene surfaces and metal atoms has received a great deal of attention. The main motivation of these studies is understanding the role of metal contacts in carbon electronics. As expected graphene is sensitive to charge transfer from metals because of the small density of states (DOS) at the Fermi energy; the valence and conduction bands of graphene touch at the Dirac point. Thus, even a very small charge transfer of 0.01 eV shifts the Fermi level by 0.47 eV [26]. In the case of physisorbed metals, the electronic structure of graphene is preserved and the charge transfer between metal and graphene is governed by the difference in their work functions [26]. In the case of chemisorption (Co, Ni, Pd, Ti) the metal adsorption perturbs the graphene bands which aquire a mixed graphene-metal character. The rehybridization between the graphene p_z and metal d orbitals opens a band gap in graphene and significantly lowers the work function, which leads to an electron transfer from the metal to graphene or n-type doping [27,28].

In the case of mono-hexahapto Cr-functionalization of graphene the charge re-distribution is more complex and it is also affected by the choice of the second ligand [$(CO)_3$, C_6H_6]; thus it can not be explained considering the interaction between the graphene and Cr ad-atoms alone. Note that the formation of a hexahapto–metal bond is distinct from the interaction of bulk metals with the graphene lattice in the sense that the metal establishes a bond to the graphene surface and not a work function with a distinct Fermi level. Our previous experiments [8] show that the e-beam deposition of Cr atoms on a single layer graphene results in a decrease of graphene conductivity, as opposed to the increase found in the current experiments; the e-beam evaporated Cr atoms do not aquire the stable 18-electron configuration. DFT calculations show that the (η^6-graphene)$Cr(CO)_6$ complexes exhibit a semiconducting feature with the d-bands of the transition metal located in the gap of graphene and a band gap that depends on the surface coverage ratio (number of Cr atoms bound to the graphene lattice) [12].

Further theoretical studies and experimental analysis, utilizing analytical tools (EXAFS, ARPES) and device characterization (FET), of the mono-hexahapto complexes of graphene are required to shed light into the electronic structure and properties of these novel materials, and it may provide new insight into the formation of contacts to carbon materials.

4. Conclusion

We have demonstrated the formation of hexahapto graphene complexes with transition metals synthesized using a facile and simple photochemical route. The graphene complexes with chromium showed significantly enhanced conductivity that ranges from 4-fold increase as in the case of the reaction with $Cr(CO)_6$ to about 2 times for the Cr(η^6-benzene)$(CO)_3$ reagent.

The organometallic chemistry of graphene offers a myriad of opportunities to the design of materials with diverse properties: from opening a band gap in graphene, to novel materials with enhanced conductivity, to the preparation of ordered magnetic materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.carbon.2017.12.025.

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