

Synthesis and XPS Characterization of Si-Supported Chromium(0) Fischer Aminocarbene complexes

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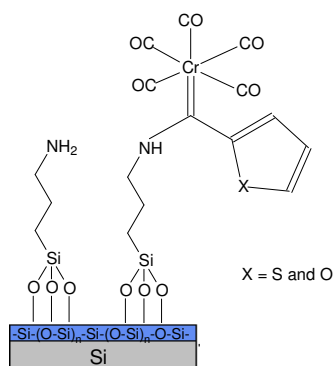
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TOC:



Keywords:

Fischer carbene complex; XPS; silane anchoring.

Highlights

- Synthesis of Si-supported amino Fischer carbenes.
- X-ray photoelectron spectroscopy of supported amino Fischer carbenes.
- Cr 2p_{3/2} binding energies of ethoxy-, amino- and Si-supported Fischer carbenes

Abstract

Ethoxy chromium (0) Fischer carbene pentacarbonyl complexes [(CO)₅CrC(OEt)R]; R = 2-thienyl (**1**), 2-furyl (**2**) were covalently anchored onto aminopropyltrimethoxysilane-functionalised silicon-wafers to form Cr-grafted Si-wafers **S1** and **S2** that were characterized by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy determined that binding energy of the Cr 2p_{3/2} photoelectron line of the thienyl-containing complexes were smaller than that of the furyl-containing complexes. The binding energy of the Cr 2p_{3/2} photoelectron line of the ethoxycarbene complexes was smaller than that of aminocarbenes. The binding energy of the Cr 2p_{3/2} photoelectron line of the Cr-grafted Si-wafers were *ca.* 1 eV higher than that of the related aminocarbenes. A 25 – 33 % anchoring of the Cr-complexes **1** and **2** on the aminopropyltrimethoxysilane-functionalised silicon-wafers was achieved.

1. Introduction

Fischer-type carbene complexes (FCCs) have been the interest of many synthetic,¹ structural,² electrochemical, electronic, theoretical and spectroscopic studies.^{3-10,11,12} In particular, Fischer carbene complexes of chromium have found application in a variety of different organic transformations,¹³ cyclization reactions,¹⁴ metal-templated conversions,¹⁵ benzannulation reactions¹⁶ and are particularly useful in the activation of organic molecules.¹³ The applicable mechanisms in the syntheses and reaction mechanisms of FCCs in organic reactions are typically explored by quantum chemical calculations¹⁷ and in addition to yielding organic products, substrate-carbene interactions afford numerous novel coordination complexes.¹⁸

Heterogeneous materials can be more easily recovered and recycled from reaction solutions than homogeneous materials. Therefore, the possibility of incorporating FCC complexes onto a solid support to yield heterogeneous materials may lead to new applications

of FCCs in the future. The grafting of FCCs on solid surfaces is ill-explored in literature. Ojeda et al. covalently tethered a W-Fischer carbene complex into the ordered mesoporous MCM-41 channels,¹⁹ as well as onto a SBA-15²⁰ surface. Dutta et al. anchored alkoxy Fischer carbene complexes on glass/silicon surfaces to provide an anchoring site for proteins (Figure 1).^{21,22}

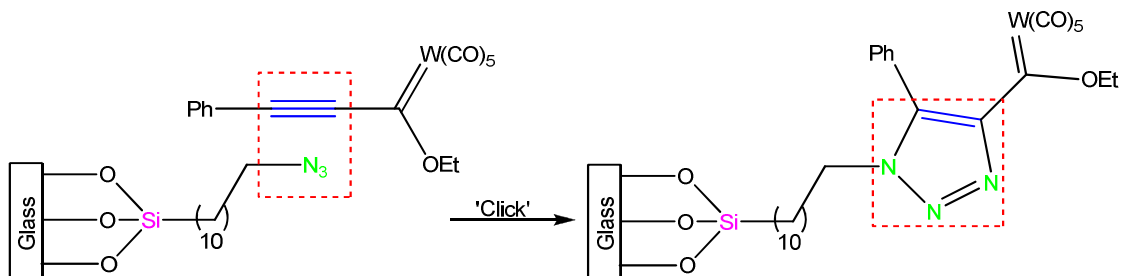


Figure 1: Grafting of FCCs on solid surfaces

In this study, the scope of anchoring FCCs to solid supports is expanded by anchoring chromium Fischer carbene complexes *via* an amine-silane linker onto a silicon wafer. The successful anchoring of the Cr-Fischer carbene complexes is confirmed with X-ray photoelectron spectroscopy (XPS). Characterisation of Fischer carbene complexes with X-ray photoelectron spectroscopy (XPS) is not well known. XPS of the C 1s peak was utilized to determine the relative importance of the resonance structures of $[(CO)_5CrC(OCH_3)(CH_3)]$.²³ A recent XPS study of a series of penta-, tetra- and tricarbonyl Mo-Fischer ethoxycarbene complexes showed that a decrease in the amount of carbonyl groups are associated with a decrease in the binding energy of the Mo 3d photoelectron lines and an increase in the binding energy of the carbene carbon C 1s photoelectron lines.²⁴ It would thus be of interest to determine the influence of an N (amino group) relative to an O (ethoxy group) as heteroatom on the binding energy of the metal and carbene C in Cr-Fischer carbene complexes.

An X-ray photoelectron spectroscopic (XPS) study for a series of four ethoxy and cyclohexylamine Cr-Fischer carbene pentacarbonyl complexes of general formula $[(CO)_5CrC(OEt)R]$ and $[(CO)_5CrC(NHCy)R]$ with R = 2-thienyl or 2-furyl is thus reported in this study. The two ethoxy-containing Fischer carbene complexes were anchored via an amine-silane linker onto a silicon wafer to prepare a 2-dimensional supported Fischer carbene complex which could have a potential application as an anchoring site for proteins.^{21,22}

2. Experimental

2.1. General

All syntheses were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen or argon gas.²⁵ Solvents were dried prior to use. Chromatographic separations and purification were performed using nitrogen gas saturated kieselgel (0.063–0.200 mm). Thiophene was purified as described in literature, prior to use.²⁶ Triethyloxonium tetrafluoroborate was prepared according to a literature procedure.²⁷ The carbene complexes were synthesized according to known literature methods: $[\text{Cr}(\text{CO})_5\text{C}(\text{OEt})(\text{Th})]$ (**1**), $[\text{Cr}(\text{CO})_5\text{C}(\text{OEt})(\text{Fu})]$ (**2**), $[\text{Cr}(\text{CO})_5\text{C}(\text{NHCy})(\text{Th})]$ (**3**), and $[\text{Cr}(\text{CO})_5\text{C}(\text{NHCy})(\text{Fu})]$ (**4**).²⁸ Characterization data of **1–4** were in agreement with literature reports.^{11,32} Silicon wafers from Topsisil, are n-type, single crystalline with a (100) orientation, and a resistivity of 370–410 $\Omega\cdot\text{m}$.

2.2. Synthesis of supported FCC's S1 and S2

2.2.1. Preparation of Si-wafers with amino groups

The hydroxylation of the (100) silicon wafers was achieved using known reported procedures.²⁹ Firstly the silicon wafer (a ca. 1.5 cm x 1.5 cm piece) was calcined at 750 °C for 24 h in air. This afforded an amorphous -O-Si-O- layer over the Si metal with a ca. thickness of 90 nm. Following calcination, the oxidised Si-wafer was immersed in a 1:1 (v/v) H_2O_2 (25% solution) and NH_4OH (35% solution) solution at room temperature. The Si-wafer was then hydroxylated by submerging it into doubly distilled boiling water for 1 h. It was then left to air dry for 16 h. Treatment of Si-wafers in this manner, produces a surface with 4–6 -OH functional groups / nm^2 .³⁰

Subsequently, the hydroxylated Si-wafers was submerged into a mixture of 3-aminopropyltrimethoxysilane (250 mg) in dried toluene (10 ml). The solution was gently stirred for 60 h, avoiding scratching of the Si-surface, with the magnetic stirrer. Following the stirring the amino-functionalized Si-wafer, it is washed with isopropanol (3 x 20 ml) by sonication, and dried under a stream of nitrogen.

2.2.2. Covalent binding of 1-2, onto aminated silicon wafers

The newly prepared amino-functionalized wafers were submerged in a 5×10^{-1} mol.dm⁻³ solution of either **1** or **2**, in THF. The carbene/THF solution was gently stirred for 24 h with the magnetic stirrer while care was taken not to scratch the Si-surface. The amino-functionalised wafer was removed from the solution, followed by rinsing it three times with isopropanol (10 ml) and drying under a stream of nitrogen.

2.3. X-ray photoelectron spectroscopy

XPS data was recorded on a PHI 5000 Versaprobe system, with a monochromatic Al K α X-ray source. Spectra were obtained using the aluminium anode (Al K α = 1486.6 eV) operating at 50 μ m, 12.5 W and 15 kV energy (97 X-ray beam). The instrument work function was calibrated to give a binding energy of 284.8 eV for the lowest binding energy peak of the carbon 1s envelope, corresponding to adventitious carbon, which is not affected by neighbouring atoms. The spectra have been charge corrected to this main line of the C-C carbon 1s spectrum, of the adventitious carbon which was set to 284.8 eV. The survey scans were recorded at constant pass energy of 187.85 eV and detailed region scans of C 1s and O 1s at constant pass energy of 29.35 eV, while the Cr 2p, S 2p and N 1s was recorded at constant pass energy of 93.90 eV with the analyser resolution ≤ 0.5 eV. The resolution of the PHI 5000 Versaprobe system is FWHM = 0.53 eV at a pass energy of 23.5 eV and FWHM = 1.44 eV at a pass energy of 93.9 eV. The background pressure was 2×10^{-8} mbar. The XPS data was analysed utilising Multipak version 8.2c computer software,³¹ and applying Gaussian–Lorentz fits (the Gaussian/Lorentz ratios were always >95%).

3. Results and Discussion

3.1 Synthesis

Since the ethoxy moiety of complexes **1** and **2** can easily be substituted by an amino group to afford their amino-containing counterparts complexes **3** and **4**,³² it was also possible to anchor the ethoxy-containing Fischer carbene complexes **1** and **2** onto an amine-capped Si-wafer. Complexes **1** and **2** were grafted onto a 3-aminopropyltrimethoxysilane functionalised SiO₂/Si-wafer to produce **S1** and **S2** modified Si-wafers respectively (Figure 2). Before grafting of the carbene complexes **1** and **2**, the two-dimensional silicon wafer was modified

to contain amine groups. Activation of a two-dimensional silicon wafer with a (100) surface orientation starts by thermal oxidation to produce a surface layer of ca. 90 nm amorphous -O-Si-O-. Hydroxylation of the surface liberates ca. 4-6 silanol (Si-OH) groups per nm², to become hydrophilic.^{33,34} Finally, silanation of the Si-OH groups on the surface with 3-aminopropyltrimethoxysilane,³⁵ generated the amine-capped silicon wafer.³⁶ The reaction between the amine-capped silicon wafer and **1** and **2** respectively, produced surfaces **S1** and **S2** (Figure 2). Surfaces **S1** and **S2** were characterized by XPS as described in section 3.2.

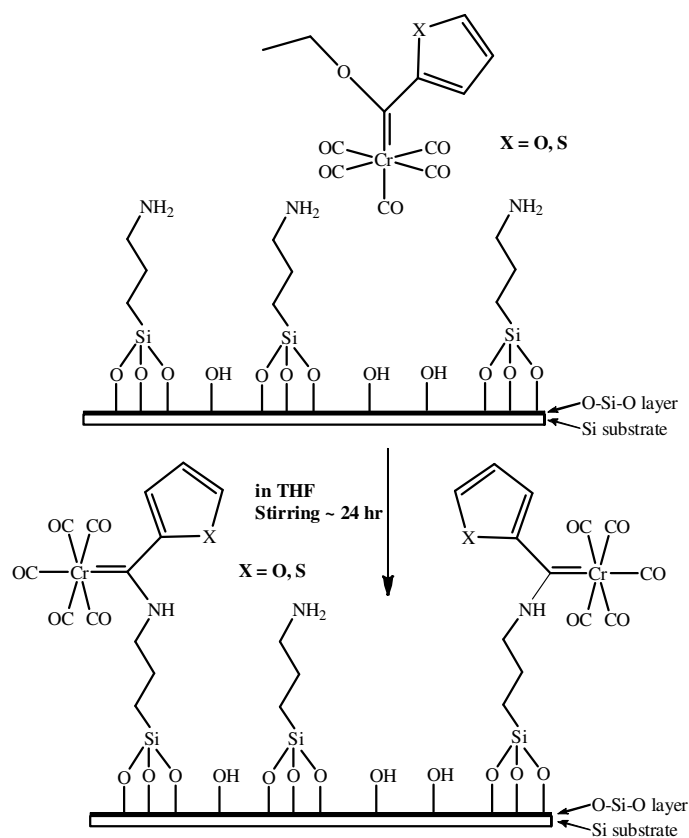


Figure 2. The chemical grafting of [Cr(CO)₅=C(OEt)(Th)], **1**, and [Cr(CO)₅=C(OEt)(Fu)], **2**, Fischer carbene complexes onto an amine-functionalized Si-wafer to form Cr-grafted Si-wafers **S1** (X = S) and **S2** (X = O).

3.2 XPS study

The unsupported carbenes **1-4** and the supported carbenes **S1-S2** were characterized by X-ray Photoelectron Spectroscopy (XPS). XPS is a well-established surface analysis

technique that provides elemental and chemical state information from the outer 5 to 10 nm of a solid surface, but is also a very useful tool to investigate powdered samples. An XPS spectrum provides core level binding energies of the elements in the sample. These binding energies are sensitive to the chemical environment of the atom. For example, the core electrons of atoms bound to strongly electron withdrawing groups will have increased binding energies and *vice versa*.³⁷

The main photoelectron lines which could be detected in the XPS spectra of the chromium Fischer carbene complexes, **1-4**, are of C 1s (with a maximum binding energy of the adventitious carbon-carbon bonds at ca. 284.8 eV), O 1s (ca. 528.8 eV) and Cr 2p (between 574-590 eV). However, complexes **1** and **3** also exhibited an S 2p photoelectron lines (S 2p_{3/2} and S 2p_{1/2} at 163.9 and 164.5 eV respectively, with a spin orbit splitting of 1.18 eV between the S 2p_{3/2} and S 2p_{1/2} photoelectron lines), while complexes **3** and **4** showed an N 1s photoelectron line at ca. 399.7 eV. The atomic ratios of the different elements obtained from XPS of **1**, **3-4**, gave the expected ratios of 1:1 (Cr:S) for **1**, 1:1:1 (Cr:N:S) for **3** and 1:1 (Cr:N) for **4**. The XPS data of the C 1s (the carbene carbon, $\underline{\text{C}}=\text{Cr}$) and Cr 2p_{3/2} photoelectron lines measured of **1-4**, are summarized in Table 1.

The Cr 2p_{3/2} photoelectron lines of **1-4**, located at between 574-576 eV, gave well-defined single peaks, with a shake-up peak at ca. 3 eV higher (see Figure 3). The spin orbit splitting between Cr 2p_{3/2} and Cr 2p_{1/2} is 9.8 and 10.55 eV for **1-2** and **3-4** respectively. The Cr 2p photoelectron lines was deconvoluted, with a single Gaussian peak with a full width at half maximum (FWHM) of ca. 2 eV for **1-2** and ca. 4 eV for **3-4**. The asymmetric index, α , (which is the ratio of the half width at half maximum on the high energy side to the half width at half maximum on the low energy side) of the Cr 2p_{3/2} for **1-2** and **3-4** are ca. 1.24 and 1.72 respectively. The broadening effect of the cyclohexylamine group on the FWHM of the Cr 2p photoelectron is very clear. This result is consistent with presence of different isomers (the *syn,Z*; *anti,Z*; *syn,E* and *anti,E* isomers as shown by an NMR and DFT study on pentacarbonyl Cr-Fischer aminocarbene complexes **3** and **4**³²), having slightly different binding energies and causing this broader photoelectron line.

Comparison of the Cr 2p_{3/2} binding energies of the ethoxy-functionalised chromium Fischer-carbene complexes, **1-2**, revealed that **2** (the furyl-containing complex) had a binding energy of 0.25 eV higher than that of **1** (the thienyl-containing complex). Similar to **1-2**, in the series of cyclohexylamine-functionalised chromium Fischer-carbene complexes, the furyl-containing complex **4**'s binding energy was found to be 0.24 eV higher than that of **3**

(the thienyl-containing complex). Substitution of the ethoxy group (O-containing) with cyclohexylamine (N-containing) resulted in *ca.* 1.3 eV higher binding energies for the Cr 2p photoelectron lines (Table 1). The order of increasing Cr 2p_{3/2} binding energy (in eV) for **1** – **4** is thus:

[Cr(CO)₅=C(OEt)(Th)], **1** (577.50) < [Cr(CO)₅=C(OEt)(Fu)], **2** (577.62) < [Cr(CO)₅=C(NHCy)(Th)], **3** (578.35) < [Cr(CO)₅=C(NHCy)(Fu)], **4** (578.53)

Generally it is found that the binding energy of a metal-electron increases as the ligands attached to the metal become more electronegative (withdraws more electron density away from the metal),³⁷ causing the metal to bind more tightly to its own electron which leads to the higher binding energy of the metal-electron. Here we obtained the opposite trend, since the thienyl ring of the carbene ligand is more electron withdrawing than the furyl ring,³⁸ and the Huheey group electronegativity of an amino group (2.61) is higher (more electron withdrawing) than that of an ethoxy group (2.51) on the carbene ligand.³⁹ We previously found that the trend over a small binding energy range (1 eV) deviates from the general trend obtained over a large binding energy range (4.4 eV).²⁴ We conclude that the binding energy range measured for **1** - **4** is too small to interpret the differences in binding energies.

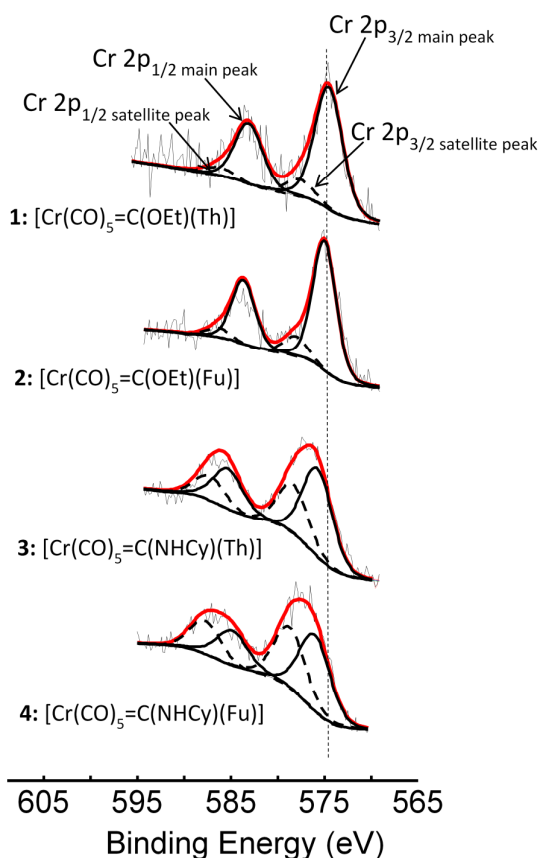


Figure 3. Comparative XPS spectra of the Cr 2p area of chromium Fischer carbene complexes, **1-4**.

The observed satellite peaks (due to the shake-up mechanism), which are c.a. 3 eV higher than the main Cr 2p peaks, are attributed to charge transfer⁴⁰ from the ligands (here most possibly a combination of the CO groups and the ligands attached to the carbene carbon) to the chromium metal. A larger satellite charge transfer peak indicates that more charge (electron density) is transferred from the ligand to the metal. The ratio of the intensities of the satellite and main Cr 2p_{3/2} photoelectron lines, $I_{ratio} = (I_{Cr2p3/2satel})/(I_{Cr2p3/2main})$, is a good indication of the amount of charge transferred from the ligand to the metal.⁴¹ The order of amount of charge transferred (from high to low) of the Fischer carbenes is: $[Cr(CO)_5=C(NHCy)(Fu)]$, **4** (with $I_{ratio} = 0.83$) > $[Cr(CO)_5=C(NHCy)(Th)]$, **3** (with $I_{ratio} = 0.57$) > $[Cr(CO)_5=C(OEt)(Fu)]$, **2** (with $I_{ratio} = 0.16$) > $[Cr(CO)_5=C(OEt)(Th)]$, **1** (with $I_{ratio} = 0.15$).

The carbon C 1s photoelectron line of **1-4**, displayed three distinct C peaks: the carbonyl carbons (C=O) at ca. 289 eV, the C-C carbons at 284.8 eV and the chromium

carbene carbon (C=Cr), located at ca. 282 eV. The position of the binding energy peak of the carbene carbon is also dependant on the different functional groups (ethoxy, cyclohexylamine, furyl and thienyl), which causes a binding energy range of 0.89 eV for the carbene carbon for complexes **1-4** (Table 1). The trend of increase in the $\underline{\text{C}}=\text{Cr}$ 1s binding energy is opposite to the trend in the increase in the Cr 2p_{3/2} binding energies of **1-4**.

The XPS spectra of surfaces **S1** and **S2** showed, in addition to the Cr, C, N, O and S peaks, also Si peaks. The Si 2p peaks the XPS of both the grafted samples **S1** and **S2** could be fitted with three peaks between 100.5 – 104.3 eV, see Table 1 and Figure 4, bottom right. The deconvoluted silicon peak located at the lowest binding energy (100.56 eV) is assigned to -O-Si-CH₂- of the silane (amine group).⁴² The second peak at 102.09 eV is attributed to the hydroxyl bound silicon atom -O-Si-OH, while the last peak at 104.28 eV is related to -O-Si-O- on the surface.⁴³ This assignment is in agreement with previously published work.³⁶ The ratios obtained between the different Si peaks are approximately 1: 1.9: 0.6 (-O-Si-CH₂-: -O-Si-OH: -O-Si-O). This implies that for every amine-functionalized silane group there are ~2 unbound Si-OH groups. Since there are 4-6 silanol (Si-OH) groups per nm^{2,33,34} there are 2-3 bound silane moieties per nm².

The nitrogen (N 1s) photoelectron line of **S1** and **S2** is resolved into two distinct peaks (Figure 4, top right). The peak at the higher binding energy (402.34 eV) is assigned to the unreacted amine-functionalized silane groups on the surface.⁴⁴ The N 1s peak located at the lower binding energy (398.28 eV) is allocated to the amine group covalently bound to the Fischer carbene complexes. For surface **S1** the ratio between the bound and unbound nitrogen is 1:3.1, therefore for every bound amine group there are ~3 amine groups not bound. A ~25% anchoring of the Cr-complexes **1** was thus achieved. For complex **S2**, however the ratio 1:2.3 was found, implying for every one amine group bound to a [Cr(CO)₅=C(OEt)(Th)], **2**, carbene complex there are ~2 unbound amine groups giving a ~33 % anchoring of Cr-complex **2**.

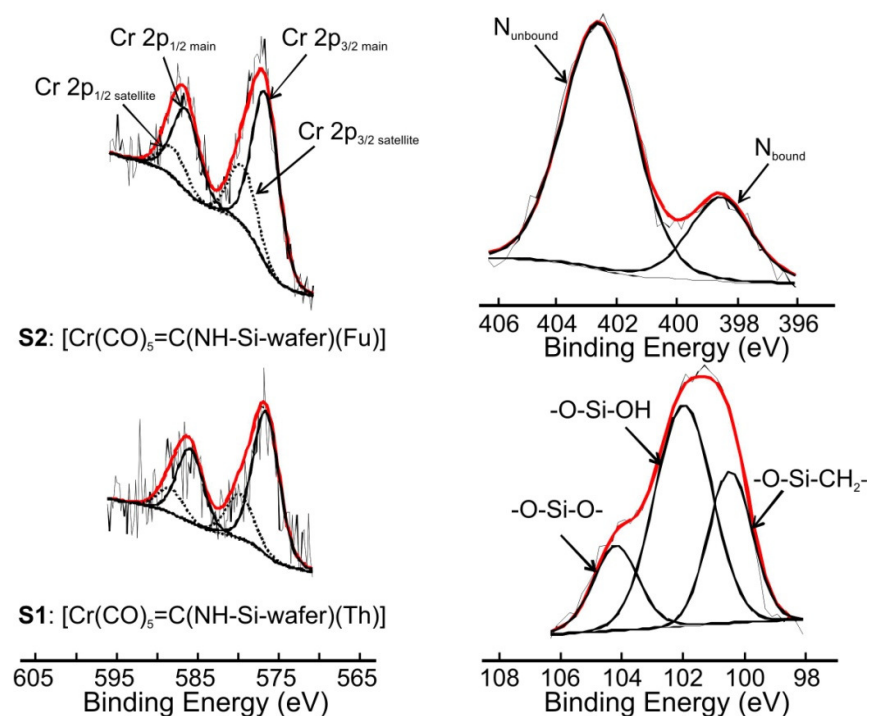


Figure 4. The deconvolution of the XPS photoelectron lines of the grafted samples **S1** and **S2** of the Cr 2p photoelectron lines (left), N 1s photoelectron lines (top right, **S1** shown, **S2** is similar) and Si 2p photoelectron lines (bottom right, **S1** shown, **S2** is similar).

Table 1. The binding energies (eV) of Si, N and Cr of the Fischer carbene complexes, neat as well as grafted onto amine-functionalized Si-wafers. Chromium coverage in Cr molecules per nm^2 .

Complex	Si 2p ^a		N 1s		Cr		$\underline{\text{C}}=\text{Cr}$	Cr / nm^2
	eV	%	eV	%	2p _{3/2} main	2p _{3/2} satel		
1: [Cr(CO) ₅ =C(OEt)(Th)]					574.33	577.50	282.94	
2: [Cr(CO) ₅ =C(OEt)(Fu)]					574.58	577.62	282.60	
3: [Cr(CO) ₅ =C(NHCy)(Th)]			400.1		575.62	578.35	282.32	
4: [Cr(CO) ₅ =C(NHCy)(Fu)]			399.3		575.86	578.53	282.05	
S1: [Cr(CO) ₅ =C(NH-Si-wafer)(Th)]	100.56 ^b	28.5	398.29 ^e	30.6	576.52	579.65		0.5-0.7
	102.09 ^c	54.1	402.34 ^f	69.4				
S2: [Cr(CO) ₅ =C(NH-Si-wafer)(Fu)]	104.28 ^d	17.4	398.29 ^e	24.4	576.82	579.75		0.6-0.9
			402.34 ^f	75.6				

^a Si photoelectron line data holds for both **S1** and **S2**. ^b Silicon atom in the amine group (-O-Si-CH₂-). ^c Silicon atom bounded to hydroxyl group (-O-Si-OH). ^d Silicon in the -O-Si-O-layer on the surface. ^e Amine bound Fischer carbene. ^f Unreacted amine group

The XPS data of the main Cr 2p_{3/2} photoelectron lines of the surfaces **S1** and **S2** (Figure 4 left) revealed that the binding energy of furyl-containing surface, **S2**, were located at 0.3 eV higher binding energies than the thienyl-containing surface, **S1** (Table 1), the same trend that was found for thienyl-containing carbene compound **1** relative to **2** the furyl-containing carbene compound and thienyl-containing carbene compound **3** relative to furyl-containing carbene compound **4**.

The main Cr 2p_{3/2} binding energies of the grafted surfaces **S1** and **S2** (576.52 and 576.82 eV respectively), which are *ca* 2.3 eV higher than the ethoxy-functionalized complexes **1** and **2**, are an indication that grafting did occur. An increase of *ca* 1.3 eV in the Cr 2p_{3/2} binding energy was obtained when comparing the aminocarbenes **3** and **4** to **1** and **2**. The Cr 2p_{3/2} binding energy of the surfaces **S1** (576.52 eV) and **S2** (576.82 eV) is *ca* 1 eV higher than the free amine-complexes **3** (575.62 eV) and **4** (575.86 eV). The shifting towards higher binding energies in going from ethoxycarbenes, to aminocarbenes to Si-supported carbenes is illustrated in Figure 5.

The ratio of the intensities of the satellite and main Cr 2p_{3/2} photoelectron lines, $I_{ratio} = (I_{Cr2p3/2satel})/(I_{Cr2p3/2main})$, for surfaces **S1** (0.31) and **S2** (0.33) is within experimental error the same but much lower than the unsupported complexes **3** (0.57) and **4** (0.87). This indicates that when bound to a Si-wafer, the charge transfer from the ligand is not as strong as when the compound is free.

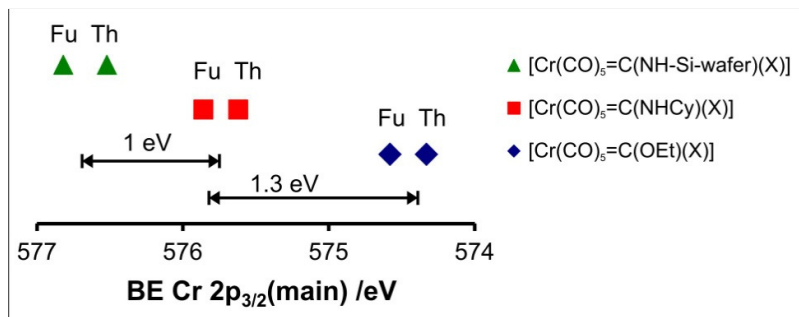


Figure 5. Comparison of the main Cr 2p_{3/2} binding energies of ethoxy-functionalized complexes **1** and **2**, aminocarbenes **3** and **4** and the Si-supported carbenes **S1** and **S2**. X = Th or Fu.

4. Conclusion

It has been demonstrated that ethoxy-containing chromium Fischer carbene complexes can be readily anchored via an amine-silane linker onto a silicon wafer by aminolysis. These immobilized chromium Fischer carbene complexes appear to be suitable for potential solid phase chemistry or as an anchoring site for proteins.

XPS characterisation of the unsupported carbenes **1-4** revealed that the furyl containing Fischer carbenes' Cr 2p photoelectron lines have a higher binding energy than the thienyl-containing Fischer carbenes. The ethoxy-containing Fischer carbenes' Cr 2p photoelectron lines appear at the lowest binding energies followed by the amino-containing carbenes. The supported Fischer carbenes were found to have the highest binding energy for the Cr 2p photoelectron lines. XPS also revealed that the order of amount of charge transferred (from the ligands to the Cr metal centre) during photo excitation of the Fischer carbenes is: $[\text{Cr}(\text{CO})_5=\text{C}(\text{NHCy})(\text{Fu})]$, **4** > $[\text{Cr}(\text{CO})_5=\text{C}(\text{NHCy})(\text{Th})]$, **3** > $[\text{Cr}(\text{CO})_5=\text{C}(\text{OEt})(\text{Fu})]$, **2** > $[\text{Cr}(\text{CO})_5=\text{C}(\text{OEt})(\text{Th})]$, **1**.

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