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Research paper

Spectroscopic characterisation of Grubbs 2nd generation catalyst and its *p*-cresol derivatives



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<i>Keywords:</i> Grubbs 2nd generation <i>P</i> -cresol XPS UV-vis FTIR	<i>p</i> -Cresol derivatives of the Grubbs 2nd generation catalyst were prepared with either hydrogen bonds between <i>p</i> -cresol and the Cl-ligands or ligand exchange between the Grubbs 2nd generation catalyst and thallium <i>p</i> -cresolate to form Ru-O coordination bonds and TlCl. ATR FTIR and UV–Vis spectroscopic studies revealed a blue shift in certain bands, indicating that coordination occurred. X-ray Photoelectron Spectroscopy was recorded for each of the three Ru-complexes. The binding energy of the Ru 3d _{5/2} , Ru 3p _{3/2} photoelectron line (found at ca. 281 and 462 eV, respectively) of the different complexes showed the influence of the inductive electronic effects of the <i>p</i> -cresol interaction with the complexes. The Cl 2p photoelectron lines indicated ionic and covalent environments, representing the TlCl and the Ru-Cl bonds, respectively. The atomic ratio between Ru:P:Cl:N:Tl confirmed the binding modes of <i>p</i> -cresol to the Grubbs 2nd generation catalyst

1. Introduction

Ruthenium-based Grubbs catalysts are extensively being used for a variety of olefin metathesis reactions (e.g. ring-closing, ring-opening, cross- and self-metathesis) under mild conditions [1–5]. The influence of different ligands or the variation of functional groups within the Grubbs catalyst on olefin metathesis is an open area of investigation. Investigation into the electronic properties (imposed by the different ligands and variation of functional groups) of the ruthenium centre is thus of importance.

The Grubbs 1st generation catalyst is a stable complex exhibiting a deformed square pyramidal crystal structure, with the apical position being occupied by the carbene carbon [6]. The Grubbs 2nd generation catalyst is a modified version of the Grubbs 1st generation catalyst, where the more labile tricyclohexylphosphine (PCy₃) ligand is replaced by 1,3–bis(2,4,6–trimethylphenyl)imidazolinium (H₂IMes, an *N*-heterocyclic carbene ligand), which is a stronger σ-donor.

Normally the addition of small quantities of additives either poisons the catalyst or have an inhibitory effect on the catalytic process. However, unexpectedly, it has been reported that the addition of phenol to the reaction mixture had a positive effect on metathesis and crossmetathesis catalysed by the Grubbs 1st and 2nd generation catalysts [7,8]. Forman, Tooze and co-workers [7] postulated that phenols may

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capture PCy₃ after the dissociation thereof from the catalyst, whereas hydrogen bond formation between the phenol and the chloride ligands was proposed to increase the electrophilicity of the carbene [7]. The Fogg group [9,10] furthermore established that free PCy₃ ligand is involved in 1,4-addition reactions with acrylates. The formed enolates were proposed to deprotonate the metallocyclobutane and *p*-cresol was suggested to protect the catalyst against decomposition by quenching the highly basic enolates through protonation. Using a phenol-functionalized polymer resin instead of free phenol, also resulted in improved catalytic performance [11].

It may therefore be contemplated that, apart from the formation of hydrogen bonds with the chloride ligands, one or both of the chloride ligands of the catalyst may be substituted by *p*-cresol or *p*-cresolate. Aryloxy ligands with electron-withdrawing substituents are known to form σ -bonds with ruthenium, whereas π -interactions and the formation of piano-stool complexes predominates in the absence of electron-withdrawing groups or *ortho* substituents [12–14]. The σ - π isomerisation could be circumvented by various authors by making use of bidentate aryloxy ligands [2,15–20].

Known monodentate aryloxy complexes of ruthenium benzylidenes seem to be limited to those with electron-withdrawing halogen substituents on the aryloxy ligand and pyridine ligands for further stabilisation, e.g. $Ru(OC_6F_5)_2(CHPh)(IMes)(py)$ [21–24] or aryloxy ligands

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with *ortho* substituents such as $Ru[O(2,6-Me_2C_6H_3)]Cl(PCy_3)(=CHPh)$ [25], $Ru[O(2,6-Ph_2C_6H_3)]Cl(PCy_3)(CHPh)$ or $Ru[O(2-PhC_6H_4)]Cl(PCy_3)$ (CHPh) [26]. Ruthenium aryloxy benzylidenes such as RuCl(OPh)(PCy_3)₂(CHPh) and $Ru(OPh)_2(PCy_3)_2(CHPh)$ are short-lived and have only been observed in situ [27]. Bisphenoxy derivatives of the first generation Grubbs catalyst were reported to decompose into the corresponding alkylidynes, e.g. $Ru(OPh)(PCy_3)_2(CPh)$ [22–24,27]. These generalizations may be influenced by the steric bulk and electronic properties of the other ligands in the complex, though [24].

With this in mind, the possibilities of factors to be considered in the investigation of the electronic properties of the ruthenium centre are even more interesting and important.

Herein we spectroscopically characterise and examine the electronic properties of the Grubbs 2nd generation catalyst and two of its *p*-cresol derivatives with NMR, ATR FTIR, UV–Vis and X-ray photoelectron spectroscopy (XPS), the latter being a very useful technique to gain insight into the electronic properties of the core electrons of compounds.

2. Experimental

2.1. Materials and general procedures

The Grubbs 2nd generation catalyst ((1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium), **1**, and other solid and liquid reagents such as thallium ethoxide used in preparations were purchased from Sigma-Aldrich, and were used without purification. *Caution*: All thallium compounds should be handled with precautions and care, since it is extremely toxic.

Solvents were dried over sodium wire while refluxing under argon or filtered through a small column of activated neutral alumina (10% v/v) prior to use.

2.2. Spectroscopic measurements

¹H and ¹³C NMR measurements were recorded on a Bruker AVANCE II 600 FT NMR spectrometer and ³¹P NMR on a 400 MHz AVANCE III spectrometer at 298 K. The chemical shifts are reported relative to SiMe₄ at 0.00 ppm for ¹H and ¹³C NMR and relative to phosphoric acid for ³¹P NMR. HMBC and HSQC was used to assign the NMR signals. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra were recorded on a Thermo Scientific IR spectrometer with a NICOLET iS50 ATR attachment, and UV–Visible (UV–Vis) spectra were recorded as a 0.2 mM solution in acetonitrile on a Cary 50 Probe UV/ Visible spectrophotometer.

2.3. Synthesis

2.3.1. Grubbs II – p-cresol catalyst, 2

Grubbs second generation catalyst (1) (100 mg, 0.12 mmol) and *p*cresol (26 mg, 0.24 mmol, 2 eq.) were refluxed for 1 h in dry CH₂Cl₂ (10 mL) in a glovebox. The solvent was removed in vacuo and the residu analyzed by various spectroscopic methods. The newly formed product was not purified since it decomposed during purification attempts. ¹H NMR [600 MHz, CDCl₃]: δ 19.06 (s, benzylidene carbene), 8.95 (s, H-2C), 7.35 (t, J = 7.3 Hz, H-4C), 7.15 – 6.90 (m, Ar-H), 7.00 (d, J = 8.1 Hz, cresol H-3, H-5), 6.79 (d, J = 8.4 Hz, cresol H-2, H-6), 6.70 (d, J = 8.1 Hz, H-5A), 6.15 (s, 0H), 5.79 (s, H-3A), 4.08 – 3.70 (m, NCH₂), 2.75 (s, Me), 2.55 (s, Me), 2.48 (s, Me), 2.31 (s, Me), 2.26 (s, 2x Me), 2.18 (tt, J = 14.9, 6.8 Hz, PCy-CH), 2.03 (s, Me), 1.89 (s, Me), 1.60 – 0.74 (m, PCy-CH₂);

¹³C NMR [151 MHz, CDCl₃]: δ 294.3 (benzylidene carbene), 219.9 (d, J = 76.9 Hz, C-2C), 155.7, 153.4 (cresol C-1), 153.2, 151.0 (C-1C), 139.6, 139.0 and 138.6 (C-2,6A or B), 138.4 (C-4B), 137.6 (C-4A), 137.3, 137.0, 136.6 (C-2,6B or A), 135.0 (C-1B or A), 134.8, 131.9,

130.2, 130.1, 129.9 (cresol C-3,5), 129.8, 129.7, 129.6, 129.5, 129.3, 129.2 128.8, 128.7, 128.6, 128.2, 127.6, 127.1, 126.5, 121.2, 116.3, 115.6, 115.4, 115.2, 112.6, 52.2 (d, J = 3.2 Hz, C-4), 51.3 (d, J = 1.1 Hz, C-5), 35.1, 34.7, 31.5 (d, J = 16.6 Hz, C-2,6D), 29.0 (d, J = 54.6 Hz, PCy₃-C), 27.6 (d, J = 9.9 Hz, PCy₃-C), 26.7, 26.6, 26.1, 25.9, 21.3, 21.1, 21.0, 20.8, 20.4, 20.3, 19.9, 18.5; ³¹P NMR [243 MHz, CDCl₃]: δ 28.9.

2.3.2. Grubbs II – p-cresolate catalyst, 3

A solution of thallium ethoxide (0.705 g, 2.8 mmol, 1.2 eq.) in dry THF (5 mL) was filtered through glass wool and added dropwise to a solution of *p*-cresol (0.2554 g, 2.4 mmol) in dry THF (10 mL) in an argon atmosphere. The mixture was stirred for 24 h at room temperature, whereafter it was centrifuged and the supernatant concentrated in vacuo under argon to give thallium *p*-cresolate (5) as an off-white solid (0.447g, 76%): ¹H NMR [600 MHz, C₆D₆]: δ 7.14 (2H, d. *J* = 8.2 Hz, H-3,5), 6.69 (2H, d. *J* = 8.2 Hz, H-2,6), 2.29 (3H, s, -CH₃); ¹³C [151 MHz, C₆D₆]: δ 161.9 (C-1), 130.7 (C-3,7), 125.6 (C-4), 117.5 (C-2,6), 20.8 (-CH₃).

Thallium p-cresolate (5) (72 mg, 0.24 mmol, 2 eq.) was added to 1 (100 mg, 0.118 mmol) and stirred for 48 h at room temperature in dry benzene (1 mL) under an inert atmosphere, whereafter the reaction mixture was centrifuged (9000 rpm, 16 °C, 1 h) and the supernatant concentrated in vacuo under argon to give benzylidene[1,3-bis(2,4,6trimethylphenyl)-2-imidazolidinylidene]chloro(4-methylphenoxy)ruthenium (3). The newly formed product was not purified since it repeatedly decomposed during purification attempts. The residue was analysed by various spectroscopic methods. ¹H NMR [600 MHz, CDCl₃]: δ 19.14 (s, benzylidene carbene), 16.84 (s), 16.80 (s), 9.05-8.88 (m, H-2C), 7.52 (d, J = 7.4 Hz, H-2E), 7.38-7.33 (m, ArH), 7.28-7.23 (m, ArH), 7.15-7-05 (m, ArH), 7.01 (s, H-3B), 6.97 (d, J = 7.5 Hz, cresolate ArH), 6.99–6.93 (m, cresolate ArH), 6.92 (s, H-5B), 6.84-6.69 (m, cresolate ArH), 6.72 (br s, H-5A), 5.82 (br s, H-3A), 3.99 (br s, NCH₂), 3.80 (br s, NCH₂), 2.84 - 2.40 (m, Me), 2.37 (s, 2-MeB), 2.31 (s, 4-MeB), 2.29 (s, cresolate-Me), 2.26 (s, cresolate-Me), 2.25 (s, cresolate-Me), 2.22 (s, Me), 2.22-2.14 (m, PCy-CH), 2.11-1.95 (m, 2-MeA), 1.91 (s, 4-MeA), 1.88 - 0.72 (m, PCy-CH₂); ¹³C NMR (151 MHz, CDCl₃) δ 294.5 (C-1'), 288.8 (C-1'), 220.4 (d, J = 77.6 Hz, H-2), 154.7 (C-1E), 151.3 (C-1C), 139.1, 138.4 (C-4B), 137.6, 137.2, 135.1 (C-1 Mes), 134.9 (C-1 Mes), 132.5-131.1 (C-2C), 130.1 (C-5C), 129.9 (C-3B), 129.8 (cresolate-C), 129.5, 128.7, 128.4, 127.9, 127.6, 126.5 (C-3C), 115.5 (cresolate-C), 52.2 (d, J = 3.8 Hz, C-4), 51.3 (br s, C-5), 35.2 (d, 40.1 Hz, PCy₃-C), 31.4 (d, J = 16.4 Hz, PCy₃-C), 29.0 (br d, PCy₃-C), 27.7 (d, J = 10.0 Hz, PCy₃-C), 26.8 (d = 11.6 Hz, PCy₃-C), 26.3 (d, J = 3.1 Hz, PCy₃-C), 26.1 (br s, PCy₃-C), 21.2 (4-CH₃B), 20.9 (4-CH₃A), 20.5 (CH₃), 20.0 (2,6-CH₃B), 18.7 (CH₃), 18.1 (CH₃), 18.0 (CH₃), 17.3 (CH₃)^{; 31}P NMR [161.97 MHz, CDCl₃]: 29.0.

2.4. X-ray photoelectron spectroscopy

XPS data was recorded on a PHI 5000 Versaprobe system with a monochromatic Al Ka X-ray source. Spectra were obtained with the aluminium anode (Al K α = 1486.6 eV) operating at 50 µm, 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 1 s 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 1 s 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 while the detailed region scans of the C1 s, O1 s, P 2p, Cl 2p, N1 s and Ru 3p spectra were recorded at a constant pass energy of 93.90 eV, with the analyser resolution \leq 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 eVat a pass energy of 93.9 eV. The background pressure was 2 \times 10⁻⁸ mbar. The XPS data was analysed utilising Multipak version 9.7c



Scheme 1. Preparation of Grubbs 2nd generation catalyst-*p*-cresol adduct, **2**, and the modified Grubbs 2nd generation-cresolate derivative, **3**, from the Grubbs 2nd generation catalyst, **1**, having different interactions with *p*-cresol, **4**.

computer software, [28] and applying Gaussian–Lorentz fits (the Gaussian/Lorentz ratios were always > 95%).

3. Results and discussion

3.1. Synthesis

Two derivatives of the Grubbs 2nd generation catalyst, **1**, having different interactions (bonding modes) with *p*-cresol, **4**, namely either hydrogen bonds between *p*-cresol and the chloride ligands of **1** or Ru-O coordination bonds in a *p*-cresolate modified catalyst, **3**, were prepared according to Scheme **1**. The former (**2**) was obtained from Grubbs 2nd generation catalyst, **1**, and *p*-cresol, **4**, in refluxing DCM, though the number of hydrogen bonds remain to be established.

The first step in the preparation of cresolate derivative 3, is the synthesis of thallium cresolate, 5, which involves the exchange of the ethoxide from thallium ethoxide with the p-cresolate anion. The second step involves chloride-cresolate exchange between 1 and thallium cresolate, 5, to form Ru-O bonds. This step is facilitated by the highly electrophilic character of the thallium cation (which was previously demonstrated to increase the rate of exchange when compared to alkali metal cations) and driven by the precipitation of the insoluble thallium chloride salt. [12,15,24,26] The newly prepared *p*-cresol derivatives 2 and 3 were isolated from the reaction mixture and analysed without further purification as all attempts to purify it, resulted in decomposition. This instability finds a precedent in the transient nature of the only other known ruthenium benzylidenes with simple monodentate phenoxy ligands, RuCl(OPh)(PCy₃)₂(CHPh) and Ru(OPh)₂(PCy₃)₂(CHPh). These complexes were characterized in situ and only the benzylidene proton and PCy₃ phosphorus resonances were reported. [27]

3.2. Characterisation

When the ¹H NMR spectrum (CDCl₃) of the Grubbs 2nd generation *p*-cresol catalyst, **2**, is compared with those of the Grubbs 2nd generation catalyst, **1**, and *p*-cresol, **4** (Fig. 1, spectra 1, 2 and 3), it is evident that a new species has formed. The benzylidene carbene resonance (H-1') is shifted upfield from δ 19.14 to 19.06 ppm, whereas the *p*-cresol H-2/H-6 protons are deshielded (δ 6.79 vs. 6.72 ppm) and the H-3/H-5 protons slightly shielded (δ 7.03 vs. 7.00 ppm) relative to those of *p*-cresol **4**.

No change in the phosphorous chemical shift of the PCy₃ ligand (δ_P 28.9 ppm) could be detected when the ³¹P NMR spectrum of **2** was compared to that of the Grubbs second generation catalyst, **1**, and no free PCy₃ ligand (δ_P 10.5 ppm),[29] was detected. NOE results reported elsewhere placed the *p*-cresol, PCy₃, benzylidene and H₂IMes ligands in

the proximity of the same ruthenium center.[30]

The reaction of Grubbs 2nd generation catalyst, **1**, with thallium *p*cresolate, **5**, resulted in an upfield shift of the cresolate (ring E) H-3/H-5 protons (δ 6.98 – 6.93 vs.7.055 ppm) and a downfield shift of the H-2/ H-6 protons (δ 6.83 – 6.76 vs. 6.70 ppm) relative to those of thallium *p*cresolate, **5**, thus confirming a change in the electronic environments thereof (Fig. 1, spectrum 6 vs. spectrum 4, CDCl₃). Treatment of the Grubbs 2nd generation catalyst, **1**, with 1 and 2 eq. of thallium cresolate, **5**, emphasized partial coalescence of several resonances (Fig. 1, spectra 5 and 6 with 1 and 2 eq. of thallium cresolate, respectively). Still, many of the resonances were multiplied or broadened, most probably due to chemical exchange and the presence of several conformers as a result of restricted rotation. [18,31]

Additional proof for p-cresolate - chloride exchange was found in the low field doublet at δ_H 7.52 ppm. A deshielding effect of this magnitude may be explained by the anisotropic effect of the metal on H-2 of the cresolate (indicated as H-2E') when the complex assumes a conformation with the cresolate below the plane of the square planar pyramid, as was also reported for palladium phenolate complexes.[32] The carbon to which this proton is attached (δ_{C} 126.5 ppm) showed cross peaks to H-6E' ($\delta_{\rm H}$ 7.28 – 7.23, m overlapping with CHCl₃) and H-3E' (δ_H 7.15 – 7.05 ppm, m overlapping with benzylidene proton resonances). H-3E', together with a H-5E' resonance ($\delta_{\rm H}$ 7.38 – 7.33 ppm), correlated with C-1E' (δ_{C} 137.1 ppm), whereas H-5E' correlated with C-4E' (δ_{C} 128.4 ppm, which was confirmed to be a quaternary carbon by means of a DEPT experiment and furthermore correlated to a methyl group resonating at δ_H 2.25 ppm) in an HMBC experiment, thus suggesting the cresolate moiety in this conformer to have non-equivalent environments for all protons (Table S1, Fig. S1).

The Ru = CHPh resonance at $\delta_{\rm H}$ 19.14 ppm compares well with those of RuCl(OPh)(PCy₃)₂(CHPh) and Ru(OPh)₂(PCy₃)₂(CHPh) at $\delta_{\rm H}$ 19.30 and 18.29 ppm (THF-d₈)²⁷ and those of the pseudohalides Ru (OC₆F₅)₂(IMes)(py)(CHPh), Ru(OC₆F₅)₂(IMes)(3-Br-py)(CHPh), RuCl (OC₆Br₅)(IMes)(py)(CHPh) and RuCl(OC₆Br₅)(IMes)(3-Br-py)(CHPh) between $\delta_{\rm H}$ 18.7 and 19.7 ppm. [22,23] The carbene and phosphine resonances of cyclic ruthenium phenolate **6** were reported at $\delta_{\rm H}$ 15.85, $\delta_{\rm C}$ 281.4 and $\delta_{\rm P}$ 29.1 ppm (CD₂Cl₂), [20] whereas the carbene protons and carbons of the catecholato complex Ru(κ^2 -O₂C₆H₄)(IMes)(py) (=CHPh), **7**, and the Hoveyda-type catecholate **8** (Chart 1) resonated at $\delta_{\rm H}$ 16.99 and $\delta_{\rm C}$ 287.4 ppm (CDCl₃) [12] and $\delta_{\rm H}$ 16.03 and $\delta_{\rm C}$ 265.6 ppm (CD₂Cl₂),[28] respectively.

In the case of π -bound aryloxide rings, upfield shifts of the ¹H and ¹³C NMR resonances relative to that of the free ligand are diagnostic. [12] When exposed to the Grubbs 2nd generation catalyst, **1**, the H-2/H-6 resonances of *p*-cresol, **4**, and *p*-cresolate, **5**, were deshielded and the H-3/H-5 resonances shielded, whereas the resonances of the E'-cresolate moiety were all shifted downfield, thus disproving the formation of piano-stool complexes.

NOE results reported elsewhere confirmed through space association of the benzylidene ring with the *p*-cresolate as well as the phosphine. [30]

In ³¹P NMR (CDCl₃) experiments, resonances were observed at δ_P 29.0 and 28.9 ppm for complexes **3** and **1**, as opposed to δ_P 10.5 ppm for free PCy₃, [33] thus confirming the PCy₃ ligand to still be attached to the ruthenium center.

Of paramount importance is the evidence that the species formed from Grubbs 2nd generation catalyst, 1, and thallium *p*-cresolate, 5, is clearly different from the species formed from 1 and *p*-cresol, 4, thus disproving the formation of a cresolate species such as 3 from 1 and *p*-cresol, 4.

The formation and stability of catalyst **3** under metathesis reaction conditions, as well as in-depth study of catalyst **2** and reactions thereof, will be reported in a forthcoming paper [30]

To fully describe the influence of the different interactions of the *p*-cresol, **4**, with the Grubbs 2nd generation catalyst, **1**, on its electronic properties, UV–Visible spectroscopy (UV–Vis), Attenuated Total



Fig. 1. ¹H NMR (CDCl₃) spectra of the Grubbs II – *p*-cresol catalyst, 2 (spectrum 1), Grubbs II, 1 (spectrum 2), *p*-cresol, 4 (spectrum 3), thallium *p*-cresolate, 5 (spectrum 4), Grubbs II – *p*-cresolate catalyst (1 eq. thallium cresolate) (spectrum 5), Grubbs II – *p*-cresolate catalyst (2 eq. thallium cresolate), 3 (spectrum 6). B refers to one of the mesityl rings and C to the benzylidene ring. E and E' refer to the *p*-cresolate moiety in different catalyst conformations, with E' indicating the conformation with the *p*-cresolate below the plane of the square planar pyramid.



Chart 1. Selected examples of ruthenium benzylidene complexes with aryloxy ligands.

Reflectance Fourier Transformed Infra-red (ATR FTIR) and X-ray Photoelectron Spectroscopy (XPS) were employed.

3.3. UV–Visible spectroscopy

The maximum absorbance (molar absorptivity) of the bands in acetonitrile (CH_3CN) and dichloromethane (DCM) as measured by

UV–Vis of 1–4, is summarised in Table 1 and the spectra are shown in Fig. 2 (for DCM) and the Supplementeray Information (CH₃CN). The spectra in CH₃CN and DCM are similar, however the spectra in CH₃CN displays much lower molar absorptivity, ε .

The UV–Vis spectrum of **1**, in acetonitrile showed a peak at 337 nm, while in DCM the peak was observed at 336 nm, which correlates well with the published value of 336 nm in DCM. [6] **2** shows the same absorption peak, but with a slightly lower molar absorptivity, ε . However, for **3** in both CH₃CN and DCM, the absorption peak at 337 nm is blue shifted to 310 nm, implying that the electronic structure of the complex has been modified upon coordination. In DCM, the bands appear as shoulders of the increasing background.

UV–Vis spectra of 1–3 also showed a weak absorption peak at longer wavelength. These bands are attributed to metal to ligand charge transfer (MLCT), in correlation with published reports.[34,35] The energy of the π^* orbital of the ruthenium-carbon bond decreases as

Table 1

Wavelengths at peak maxima (λ_{max}) and molar absorptivity, ε , of UV–Vis bands of 1–4 in acetonitrile, as well as some stretching and vibrational bands as measured by ATR FTIR.

No	$ \begin{array}{l} \lambda_{\max} \ (nm) \\ [\epsilon \ (M^{-1} \ cm^{-1})] \end{array} $	$C = C sp^2$ (cm ⁻¹)	C–O Phenol (cm ⁻¹)	P-C stretch (cm ⁻¹)
1	CH ₃ CN: 337 [1139]; 505 [28.44]	-	-	740
	DCM: 336 [12520]; 502 [430]			
2	CH ₃ CN: 280 [775]; 286 [816]; 336 [775]; 501 [33.54]	1511	1204	741
	DCM: 280 [10760]; 286 [10500]; 334 [12130]; 501[410]			
3	CH ₃ CN: 280 [1659]; 286 [1664.9]; 310 [1498]	1512	1204	743
	DCM: 286 [10390]; 310 [7700]; 324 [6690]; 530 [1480]			
4	CH ₃ CN: 217 [551]; 223 [639]; 280 [190]; 287 [156]	1514	1213	-
	DCM: 208 [13520]; 228 [3700]; 280 [1920]; 286 [1560]			



Fig. 2. The UV–Vis spectra of the Grubbs second generation catalyst, **1**, (blue) and the two derivatives with different interactions with *p*-cresol, **2** (pink) and **3** (green) as well as *p*-cresol, **4** (grey), all in ca. 0.1 mM solutions in DCM. Insert: Enlargement of the 400 to 650 wavenumber area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

charge is transferred from the ruthenium metal centre, which gives rise to the charge transfer band observed. [34] The coordination of the *p*-cresolate to **3** resulted in a red shift of the MLCT band from 501 nm (measured for **1**) to 530 nm, thus implying that the electrophilic character of the carbene carbon was altered.

Upon comparing the spectra of 1-3 with the spectrum obtained for *p*-cresol, **4**, it was found that the UV–Vis spectra of 2-3 show absorption bands which correspond to those found for **4**, thus indicating that a *p*-cresol chromophore is present in the samples.

Since metathesis reactions in the presence of Grubbs catalysts are normally conducted in DCM, the stability in DCM is important. Thus, the stability of **1–3** in DCM at 25 °C was followed using UV–Vis spectroscopy for 24 h. The UV–Vis spectra showing the stability, as well as the graphs used to determine the observed rate constant, k'_{obs}(decomp), for the decomposition are presented in the Supplementary Information. Grubbs 2nd generation catalyst, **1**, and **2** show similar stability, with their k'_{obs}(decomp) being $1.47 \times 10^{-4} \text{ s}^{-1}$ and $1.48 \times 10^{-4} \text{ s}^{-1}$, respectively, whereas the cresolate derivative **3**, decomposes faster with a k'_{obs}(decomp) of $2.22 \times 10^{-4} \text{ s}^{-1}$.

The ATR FTIR spectra of 1–4 are shown in Fig. 3, while wavenumbers of the C=C sp², C–O (of the phenol) and the P–C stretching frequencies are tabulated in Table 1. All three Ru-complexes 1–3 showed the P–C stretching frequency at ca. 741 cm⁻¹, thus giving additional evidence that the PCy₃ didn't dissociate from the metal complex during the preparation processes of 2 and 3. The characteristic C=C sp² and C–O (of the phenols) stretching frequencies, which is very prominent in the ATR FTIR spectrum of *p*-cresol, can also be observed in the spectra of 2 and 3. The wavenumber of the C=C sp² and C–O stretching frequencies of 2 correspond very well with that of 4, thus supporting a hydrogen bond interaction between 1 and 4 to produce 2. However, in the case of 3 both the C=C sp² and C–O stretching frequencies were blue shifted to higher wavenumbers, indicating that complexation had occurred between 1 and 4 to produce 3.



Fig. 3. The ATR FTIR spectra (in absorption mode) of the Grubbs 2nd generation catalyst, **1**, (blue) and the two derivatives with different interactions with *p*-cresol, **2** (pink) and **3** (green) as well as *p*-cresol, **4** (gray). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. X-ray photoelectron spectroscopy (XPS)

To further characterise the Grubbs 2nd generation catalyst, **1**, and its two *p*-cresol derivatives **2** and **3**, X-ray Photoelectron Spectroscopy (XPS) was conducted. Even though XPS is a surface science technique, it can also be employed to characterise compounds and complexes in powder form [36,37]. XPS is capable of determining the elemental composition and chemical states of the elements. This is accomplished by measuring the binding energies of the core level electrons of each element. The numerical value of the binding energy is sensitive towards the oxidation state and/or chemical environment of the element. When the chemical environment around the element under investigation is electron withdrawing, the binding energy of the elements is found at higher binding energy positions. An increase in the oxidation state of the element (becomes more positive) similarly results in an increase of the binding energy.

The maximum binding energy of the simulated adventitious carbon (always present on all samples), C 1 s, was set at 284.8 eV, to charge correct the binding energies of the other elements for accurate comparison between them. The photoelectron lines detected for the different Grubbs 2nd generation catalysts, 1-3, were carbon, ruthenium, nitrogen, phosphorus and chlorine. The binding energies obtained, as well as the atomic % ratio for these, are summarised in Table 2 and are all comparable to values reported in literature [6]. The comparative XPS of the C 1 s/Ru 3d area and the Ru 3p area of 1-3, is presented in Fig. 4. From the spectra of the C1 s area, the overlap of the carbon C1 s photoelectron line with the Ru 3d photoelectron line is clearly visible and due to this overlap, the Ru 3p photoelectron line was also investigated. The binding energy found for the Ru 3d_{5/2} photoelectron lines were at ca. 281 eV, which compares well with published values of ca. 280.6 eV [6]. There is a small increase in binding energy when moving from 1 (Grubbs 2nd generation catalyst) to 2 (the hydrogenbonded Grubbs 2nd generation-p-cresol catalyst) to 3 (the modified Grubbs 2nd generation-cresolate catalyst). This is due to the electron withdrawing influence of the p-cresol/p-cresolate moiety on the Ru centre. The p-cresol/p-cresolate moiety pulls electron density towards itself (the O), causing the Ru centre to be slightly electron deficient, causing it (the Ru) to bind tighter to its own electron, hence the increase in binding energy. Cresolate complex 3 experiences this electron

Table 2

The maximum binding energy of the Ru 3p, N 1 S, G 2p and P 2p photoelectron miles, as well as the atomic ratio of each
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	C 1 s	Ru 3d		Ru 3p		N Cl		Cl	1			Р		
	Ru-C	3d _{5/2}	3d _{3/2}	3p _{3/2}	3p _{1/2}	Ratio	1 s	Ratio	2p _{3/2}	2p _{1/2}	Ratio	2p _{3/2}	2p _{1/2}	Ratio
1 2 3	283.2 283.7 283.9	280.9 281.2 281.6	285.0 285.3 285.7	461.8 461.9 462.2	483.9 484.0 484.3	1.00 1.00 1.00	399.3 399.4 399.4	1.91 2.15 1.94	197.3 197.3 197.5 198.4	199.0 199.0 200.3 201.2	2.04 2.09 1.75	130.2 130.3 130.4	131.0 131.1 131.2	0.97 1.05 0.91

withdrawing effect the most since the oxygen is bonded directly to the Ru, where 2 only experiences the inductive effect.

The Ru-C_{carbene} bond is found at ca. 283.6 eV, which is higher than the values reported for carbene carbons in Fischer carbene complexes of Mo and Cr (ca. 282.4 eV) [38,39]. The binding energies of the three Grubbs 2nd generation catalysts, **1–3**, increased in the order **1** (283.2 e) < **2** (283.7 eV) < **3** (283.9 eV). This can again be attributed to the electronic influence of the *p*-cresol/*p*-cresolate moiety, as explained previously.

The Ru $3p_{3/2}$ and the Ru $3p_{1/2}$ photoelectron lines of 1–3 gave welldefined peaks, which was fitted with a single Gaussian peak having a full width at half-maximum of ca. 3.8 eV. The Ru $3p_{3/2}$ photoelectron line was located at ~462 eV, with spin orbit splitting between the Ru $3p_{3/2}$ and Ru $3p_{1/2}$ levels of 22.1 eV (see Table 2). The position of the binding energy of the Ru $3p_{3/2}$ photoelectron line is comparable to those found for other Grubbs catalysts (ca. 462.3 eV) [6].

The variation in the binding energy found for Ru $3p_{3/2}$ photoelectron lines between **1** and **3** is caused by inductive electronic effects of the *p*-cresol's interaction with the complexes. Complexes **1** and **2** have very similar values for the binding energy of the Ru $3p_{3/2}$ photoelectron line, namely 461.8 and 461.9 eV, respectively. This suggests that the charge density on the ruthenium metal centre is similar. For complex **3**, *p*-cresolate bonding occurs through the oxygen to the ruthenium. The Pauling electronegativity of oxygen ($\chi_{C0} = 3.44$) is higher than that of chlorine ($\chi_{C1} = 3.16$). Thus, in **3** more electron density is shifted towards the oxygen away from the ruthenium metal centre as compared to **1** with two Cl-ligands. This implies that Ru in **3** to bind tighter to

its own electrons, shifting the binding energy of the Ru $3p_{3/2}$ photoelectron line in **3** (462.2 eV) to higher values than found for **1** (461.8 eV). For complex **2**, with *p*-cresol hydrogen-bonded to the Clligand(s), the shift of the binding energy of the Ru $3p_{3/2}$ photoelectron line to 461.9 eV is not as significant as in **3**.

XPS spectra of the N 1 s, Cl 2p and P 2p areas of the Grubbs 2nd generation catalyst, **1**, as an example is also presented in Fig. 5. The binding energies for the other elements present in **1–3**, (N 1 s, Cl 2p and P 2p) was minimally influenced by the presence of the *p*-cresol, thus suggesting that their direct chemical environment was not significantly altered.

The N 1 s photoelectron line of the nitrogen in the imidazolidinylidene ligand was located at ca. 399.4 eV. This binding energy is slightly higher than that found for nitrogen of a cyanide ($C=\underline{N}$) ca. 398 eV [40,41], and *meso*-positioned nitrogens of a tetrabenzoporphyrin (ca. 398.6 eV), but slightly lower than that of the inner <u>N</u>H of tetrabenzoporphyrins (ca. 399.7 eV) [42].

The expected atomic percentage ratio of 1:1:2:2 between the Ru 3p, P 2p, Cl 2p and N 1 s, was obtained for 1 (experimental ratio is 1:0.97:2.0:1.91, see Scheme 1 for the structures of 1–3). The experimental atomic ratios (Ru:P:Cl:N 1:1:2:2) and the binding energies measured for 2 agree with the presence of one phosphorous atom with an electronic environment similar to that of the PCy_3 ligand of Grubbs 2nd generation catalyst, 1, and two chloride ligands with identical electronic environments to each other, but different environments to the chloride ligands in Grubbs second generation catalyst, 1. This corroborates the notion that catalyst 1 was modified in a way that involved both chloride ligands. It is, however, not possible to confirm the



Fig. 4. Left: XPS spectra of the C 1 s and overlapping Ru 3d area of the Grubbs 2nd generation catalysts, 1-3. Right: XPS spectra of the Ru 3p area of 1-3.



Fig. 5. Top row: XPS spectra of the N 1 s, Cl 2p and P 2p areas of the Grubbs 2nd generation catalyst, 1, as an example. Bottom row: The XPS spectra of the Tl 4f and Cl 2p areas of 3.

presence of the p-cresol by means of XPS due to the large C 1 s peak of the adventitious carbon.

An atomic ratio of 1:1:2:2:1 for Ru:P:Cl:N:Tl (Ru 3p, P 2p, Cl 2p, N 1 s and Tl 4f), was obtained for **3** (experimental ratio is 1:0.91:1.75:1.94:0.8). The Cl at first seems to be too high, but inspection of the Cl 2p area of **3**, see Fig. 5, indicates the presence of Cl with two different electronic environments. The peak set at 197.5 and 200.3 eV is the Cl bound to the Ru (counts for 57% of the total Cl present), while the Cl at binding energies of 198.4 and 201.4 eV can be ascribed to the TlCl salt (counts for 43% of the total Cl present). The presence of the correct ratio of Tl present in the sample confirms that the extra Cl is ionically bound to Tl. The Tl 4 $f_{7/2}$ was found at 118.8 eV, which corresponds to reported data [43]. This strongly suggests that ligand exchange between thallium *p*-cresolate, **5**, and Grubbs 2nd generation catalyst, **1**, resulted in a complex with structure **3**, as proposed in Scheme 1, together with TlCl.

Relationships between the P–C stretching frequency, λ_{max} , P 2p_{3/2}, and/or Ru 3p_{3/2} photoelectron lines photoelectron lines of **1–3** were established, see Fig. 6. A shows a directly proportional relationship between the Ru 3p_{3/2} and P 2p_{3/2} photoelectron lines (as an example, similar linear lines were obtained when correlating binding energies of different photoelectron lines). There is a decreasing electron density around the element in question (for A Ru and P) as a result of the hydrogen bonding of the *p*-cresol (in **2**) and the *p*-cresolate (in **3**) as compared to **1**. This decreased electron density around both the elements in question (for **A** Ru and P) is responsible for the linear correlation, where an increase in the binding energy of the photoelectron line for Ru $3p_{3/2}$ is associated with an increase in binding energy for the P $2p_{3/2}$ photoelectron lines.

An inversely proportional relationship is established between the P–C stretching frequency and the λ_{max} of **1–3** (see Fig. 6 B). For both P–C stretching frequency and the λ_{max} , a blue shift was observed going from **1** to **2** to **3**. Since a blue shift is associated with shorter wavelengths and an increase in frequency of the electromagnetic waves, this inversely proportional correlation is expected.

In Fig. 6 C, an increase in the binding energy of the P $2p_{3/2}$ photoelectron lines is associated with an increase in P–C stretching frequency. Since it known that an increase in binding energy is associated with a decrease in electron density, and that a blue shift is due to an increase in energy in the system, it can be stated that a decrease in electron density (around the P) is associated with an increase in energy of the P–C bond.

Fig. 6 D, shows that an increase in binding energy of the Ru $3p_{3/2}$ photoelectron lines is associated with a decrease in the λ_{max} of 1–3. As already mentioned, an increase in binding energy is associated with a decrease in electron density, whereas a decrease in λ_{max} (which is a blue shift), is due to an increase in energy. Thus an increase in energy of the whole system (since UV–Vis is due to the collective influences of all



Fig. 6. A: Relationship between the Ru $3p_{3/2}$ and P $2p_{3/2}$ photoelectron lines of 1–3. B: Relationship between the P–C stretching frequency and the λ_{max} (in CH₃CN) of 1–3. C: Relationship between the P $2p_{3/2}$ photoelectron lines and the P–C stretching frequency of 1–3. D: Relationship between the Ru $3p_{3/2}$ photoelectron lines and the P–C stretching frequency of 1–3. D: Relationship between the Ru $3p_{3/2}$ photoelectron lines and the P–C stretching frequency of 1–3. D: Relationship between the Ru $3p_{3/2}$ photoelectron lines and the λ_{max} of 1–3.

the elements present in the system) is due to a decrease in the electron density around the Ru-centre.

4. Conclusion

The ATR FTIR and UV–Vis spectroscopic characterisation techniques indicated a blue shift for a number of key stretching frequencies and absorption bands, which is confirmation that complexation occurred between *p*-cresol and the Grubbs 2nd generation catalyst. The shift of these key stretching frequencies and absorption bands were more prominent for **3**, which indicates that the structural moieties responsible for these experience the electron influence of **4** more than in **2**.

The fluctuation of the binding energy position of the C 1 s Ru-C, Ru 3d_{5/2}, Ru 3p_{3/2} photoelectron lines (as measured by X-ray Photoelectron Spectroscopy) of the three Ru-complexes give an indication of how the electronic properties of the complexes was altered during the different interactions with p-cresol. The electronic environment around the Ru-metal centre for 1 and 2 is similar as is evident from the binding energies of the Ru 3p_{3/2} photoelectron lines, indicating that the hydrogen bond with *p*-cresol has minimal effect on the electronic properties. However, substitution of chloride by p-cresolate, caused a shift of the Ru 3p3/2 photoelectron line with 0.4 eV, demonstrating the environment of the Ru-metal centre in 3 to be more electron poor than those of 1 and 2. The atomic ratio between Ru:P:Cl:N is found to be 1:1:2:2 for both 1 and 2. For 3, however a ratio of 1:1:2:2:1 for Ru:P:Cl:N:Tl is found. Scrutiny of the Cl 2p area clearly indicated two different Cl environments, ionic and covalent. The ratio between the ionic Cl and the Tl is 1:1, which then leave the Ru:Cl ratio to be 1:2, thus attesting to the proposed structure of 3. The three different spectroscopic techniques complemented each other in the determination of the structures of the cresol-modified Grubbs catalyst species.

Comparison of a number of properties showed that as the electron density on the Ru-centre decreases, due to either the inductive effect of the hydrogen bond of the *p*-cresol to Cl or the substitution of the Cl with the *p*-cresolate, the energy of the system increases.

CRediT authorship contribution statement

M.R. Swart: Investigation. Barend C.B. Bezuidenhoudt: Supervision. C. Marais: Conceptualization, Validation, Formal analysis, Writing - review & editing. E. Erasmus: Conceptualization, Validation, Formal analysis, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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