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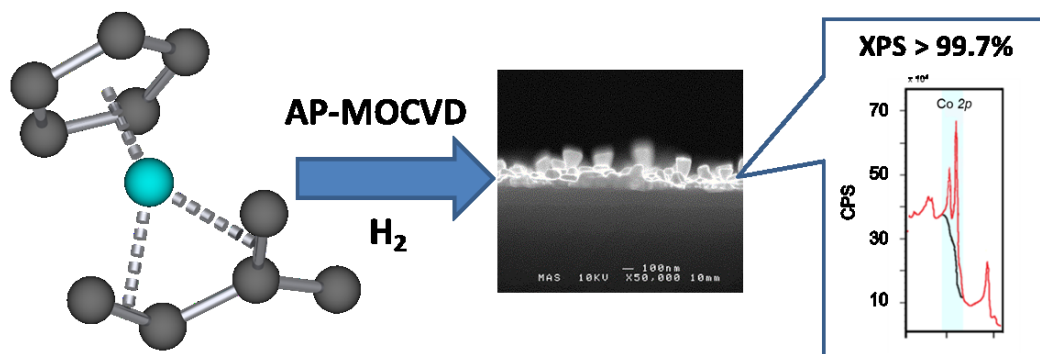
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## Table of Content Abstract and Graphic

We report the synthesis and characterization of a family of eleven cobalt (I) metal precursors based around cyclopentadienyl and diene ligands. Low pressure metal-organic chemical vapor deposition (AP-MOCVD) was employed using the precursor cyclopentadienyl-cobalt(I)(isoprene) **1**, to synthesis thin films of metallic cobalt on silicon substrates under an atmosphere (760 Torr) of hydrogen ( $H_2$ ). Thin films deposited at substrate temperatures of 325 °C, 350 °C, 375 °C and 400 °C, respectively have been analyzed by PXRD, SEM, AFM and XPS.



# Cobalt(I) olefin Complexes: Precursors for Metal-Organic Chemical Vapor Deposition of High Purity Cobalt Metal Thin Films

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## ABSTRACT:

We report the synthesis and characterization of a family of organometallic cobalt (I) metal precursors based around cyclopentadienyl and diene ligands. The molecular structure of the complexes cyclopentadienyl-cobalt(I) di-olefin complexes are described, as determined by single crystal X-ray diffraction analysis. Thermogravimetric analysis and thermal stability studies of the complexes highlighted the isoprene, dimethyl butadiene and cyclohexadiene derivatives [(C<sub>5</sub>H<sub>5</sub>)Co(η<sup>4</sup>-CH<sub>2</sub>CHC(Me)CH<sub>2</sub>)] (**1**) [(C<sub>5</sub>H<sub>5</sub>)Co(η<sup>4</sup>-CH<sub>2</sub>C(Me)C(Me)CH<sub>2</sub>)] (**2**) and [(C<sub>5</sub>H<sub>5</sub>)Co(η<sup>4</sup>-C<sub>6</sub>H<sub>8</sub>)] (**4**) as possible cobalt metal MOCVD precursors. Atmospheric pressure MO-chemical vapor deposition (AP-MOCVD) was employed using precursor **1**, to synthesize thin films of metallic cobalt on silicon substrates under an atmosphere (760 Torr) of hydrogen (H<sub>2</sub>). Analysis of the thin films deposited at substrate temperatures of 325 °C 350 °C, 375 °C and 400 °C, respectively, by SEM and AFM reveal temperature dependent growth features. Films grown at these temperatures are continuous, pin-hole free and can be seen to be composed of hexagonal particles clearly visible in the electron micrograph.

Powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS) all show the films to be highly crystalline, high purity metallic cobalt. Raman spectroscopy was unable to detect the presence of cobalt silicides at the substrate/thin film interface.

**KEYWORDS:** Cobalt, diene, Thin Films, MO-CVD

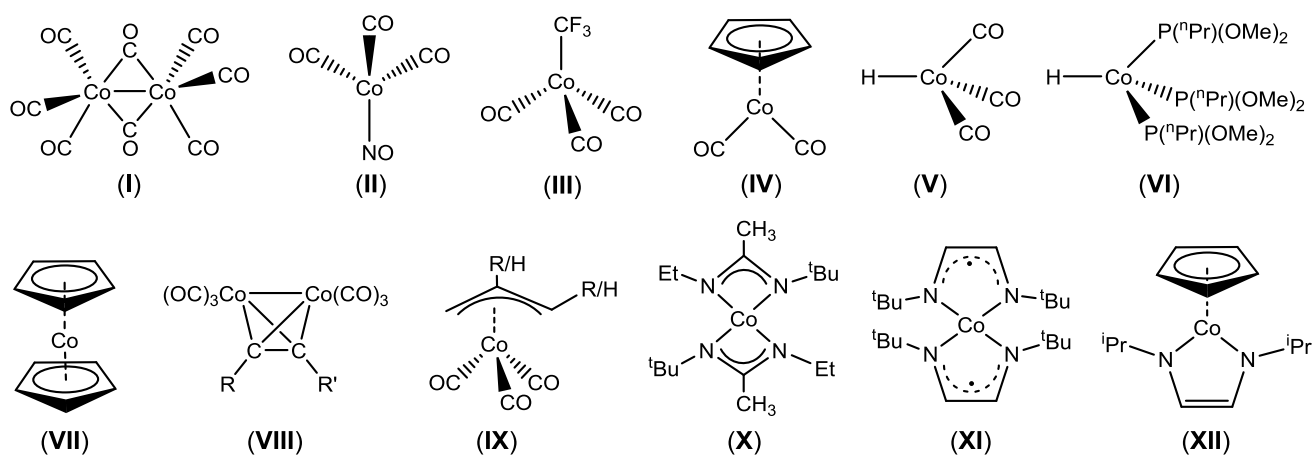
## Introduction

Cobalt is used in a wide variety of technological applications: with a higher sticking coefficient towards copper, cobalt has been used to replace tantalum as a lining material within interconnect trenches in microelectronic devices<sup>1,2</sup>. The cobalt layer allows for better copper seed layer coverage thereby reducing copper agglomeration and void formation.<sup>3</sup> Thin films of cobalt, which are ferromagnetic, may be layered with non-magnetic metals to form devices which take advantage of giant magnetoresistance (GMR).<sup>4,5</sup> These devices can be used in magnetic data storage media. Cobalt is also an important catalyst in the Fischer-Tropsch (FT) process. It has the advantage of being cheaper than ruthenium (the most active group VIII metal used in FT catalysis) and is more practical than nickel which leads to volatile carbonyl formation during the process and subsequent loss of the metal catalyst.<sup>6</sup> Typically a form of mesoporous silica<sup>7,8</sup> or alumina<sup>9</sup> is used as the support for the cobalt. Several methods of catalyst formation exist and have been reviewed.<sup>10</sup>

Previously reported preparation techniques for cobalt thin films include sputtering,<sup>11</sup> e-beam evaporation,<sup>12</sup> and thermal evaporation.<sup>13</sup> Sputtering and evaporation techniques are generally considered to be “line-of-sight” techniques, and are therefore best suited to two dimensional substrates. However, where conformal coating of three dimensional structures is desired, such as in microelectronics applications and where the trend of reduction in device sizes demands high control over these parameters, controlled formation of thin films of cobalt can be achieved using either chemical vapor deposition,<sup>2,14</sup> or atomic layer deposition.<sup>9,15</sup>

As previously noted by the authors, there are limited reports of cobalt precursors for chemical vapor deposition (CVD) or atomic layer deposition (ALD) of cobalt and cobalt oxide.<sup>16</sup> Of those reported compounds very few are liquid at room temperature, an indication that they may have an appreciable vapor pressure. High volatility is an important characteristic for both CVD and ALD precursors as it ensures that the precursor vapors are easily and consistently transported in the carrier-gas stream from the precursor vessel to the deposition chamber of the CVD or ALD system.

Metal-organic CVD (MOCVD), which uses organometallic precursors in the CVD process, offers the prospect of significantly lower deposition temperatures by virtue of the reactive, and often fragile, metal-carbon bonds. Despite this, there is a relative paucity of reports concerning organometallic cobalt precursors and especially low oxidation state species. To date thin films of cobalt metal prepared by CVD have been reported using the precursors  $[\text{Co}_2(\text{CO})_8]$  (**I**),<sup>11,17</sup>  $[\text{Co}(\text{CO})_3\text{NO}]$  (**II**),<sup>17b,18</sup>  $[\text{Co}(\text{CO})_3(\text{CF}_3)]$  (**III**),<sup>17c</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2]$  (**IV**),<sup>17a,c,19</sup>  $\text{CoH}(\text{CO})_3$  (**V**),<sup>20</sup>  $\text{CoH}[\text{}^n\text{PrOP}(\text{OMe})_2]_3$  (**VI**),<sup>21</sup>  $[(\text{C}_5\text{H}_5)_2\text{Co}]$  (**VII**),<sup>17c</sup>  $[\text{Co}_2(\text{CO})_6(\eta^2\text{-RC}\equiv\text{CR}')]$  (**VIII**) ( $\text{R}=\text{H}$ ,  $\text{R}'=\text{}^t\text{Bu}$ )<sup>22</sup> ( $\text{R}=\text{H}$ ,  $\text{R}'=\text{SiMe}_3$ ,  $\text{}^n\text{C}_4\text{H}_9$ ,  $\text{}^n\text{C}_5\text{H}_{11}$ ,  $\text{}^n\text{C}_6\text{H}_{13}$ ,  $\text{}^n\text{C}_7\text{H}_{15}$ ),<sup>23</sup>  $\text{Co}(\text{Allyl})(\text{CO})_3$  (**IX**),<sup>24</sup>  $[\text{Co}(\text{tBuNC}(\text{Me})\text{NEt})_2]$  (**X**),<sup>25</sup>  $[\text{Co}(\kappa^2\text{-}^t\text{BuNCHCHN}^i\text{Bu})_2]$ <sup>26</sup> (**XI**) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\kappa^2\text{-}^i\text{PrNCHCHN}^i\text{Pr})]$ <sup>16</sup> (**XII**) (Chart 1) at various temperatures and conditions.



**Chart 1:** Organometallic cobalt CVD Precursors.

While recent focus has been directed towards lower temperature growth methods, such as ALD and plasma assisted-ALD, in an attempt to avoid de-wetting and nanoparticle growth, precursor development has not advanced at a similar pace. Well-established “off-the-shelf” precursors such as  $[\text{Co}_2(\text{CO})_8]$ ,<sup>27</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2]$ ,<sup>28</sup>  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]$ <sup>28-29</sup> and  $[\text{Co}(\eta^3\text{-Allyl})(\text{CO})_3]$ <sup>30</sup> all originally developed for CVD, have been explored as potential precursors for ALD of cobalt metal. Only recently has there been development of new cobalt metal precursors, with the publication of the synthesis of stable and highly volatile complexes of cobalt such as the *bis*-amidinate complex<sup>25,28,31</sup> *bis*-

diazadienyl<sup>26</sup> and *bis*-hydrazonate<sup>32</sup> complexes alongside their application in the atomic layer deposition of thin films of cobalt metal and cobalt oxide.<sup>33</sup>

One family of complexes that has received almost no attention as potential precursors are cobalt(I) diolefin systems. Despite their application in catalysis cobalt(I) diolefin complexes are often thought of as highly reactive and unstable species and while this may be the case for the parent ethene system  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^2\text{-C}_2\text{H}_4)_2]$ <sup>34</sup> the use of di-olefin ligands such as butadiene, norbornadiene and 1,5-cyclooctadiene provides the complexes with significantly higher stability.<sup>35</sup> Only very recently have Lang and co-workers exploited this stability in identifying the Co(I) 1,5-hexadiene system  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2]$  as a potential cobalt MOCVD precursor,<sup>36</sup> however the related iridium complex  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Ir}(\text{COD})]$  (COD = 1,5-cyclooctadiene) has been used previously for the MOCVD production of IrO<sub>2</sub> thin films with oxygen as a co-reagent.<sup>37</sup>

Herein we report the synthesis of a range of cobalt (I) diolefin precursors, alongside studies of their thermal decomposition and volatility, and subsequent selection as suitable candidates for the MOCVD of cobalt metal films. The influence of both modification of the cyclopentadienyl and the diolefin ligand has been examined and the effect these modifications have on the physical properties such as the vapor pressure, the decomposition temperature and process as well as the deposition parameters during the MOCVD is investigated.

## ***Experimental***

### **General Experimental Details**

Tris(triphenylphosphine)cobalt(I) chloride,<sup>38</sup> and sodium cyclopentadienide and sodium methylcyclopentadienide were all made according to literature procedures.<sup>39</sup> The di-olefins used in this study were purchased through commercial sources. Compounds **3**, **4**, **5** and **6** have been synthesized previously<sup>40</sup> and <sup>1</sup>H NMR and elemental analysis was used to confirm batch purity.

General Procedures: Elemental analyses were performed by Elemental Analysis Service, London Metropolitan University, London, UK.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Advance 300 MHz FT-NMR spectrometer; chemical shifts are quoted in units of ppm, relative to  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ); coupling constants are in Hz.

All reactions were carried out under an inert atmosphere, and in the absence of light, using standard Schlenk line techniques. Low temperature reactions were performed using an ultra-low temperature recirculating chiller and modified Schlenk tube with external cooling jacket. Solvents were dried over activated alumina columns using an Innovative Technology solvent purification system (SPS) and degassed under an argon atmosphere. All other reagents were purchased from commercial sources.

## Synthesis of complexes 1-11

**Synthesis of 1:** Method A: To a THF (30 mL) solution of tris-triphenylphosphinecobalt(I) chloride (4.41 g, 5 mmol) at  $-78^\circ\text{C}$ , a 2M solution of sodium cyclopentadienyl in THF (2.5 mL, 5 mmol) was added. The solution was allowed to warm to room temperature over a period of 1 hour and was stirred for an additional hour. Isoprene (0.75 mL, 7.5 mmol) was then added and the reaction mixture was refluxed for a period of 0.5 hr, during which time a color change from deep red to red-orange was observed. The THF was removed *in vacuo* and the remaining material was extracted into hexane (3 x 20 mL) and the combined extracts were filtered through Celite®, the solvent was removed *in vacuo* and the oily residue was distilled ( $5 \times 10^{-2}$  mbar,  $50^\circ\text{C}$ ) into a liquid nitrogen cooled Schlenk yielding 0.57g (59%) of a red-orange oil.

Method B: Cobaltocene (2.2 g, 10 mmol) and potassium (0.4g 10 mmol) were dissolved in  $\text{Et}_2\text{O}$  and stirred at  $-60^\circ\text{C}$  for 6 hrs. Isoprene (1.5 mL, 15 mmol) was added dropwise to the stirred solution and the brown reaction mixture stirred for 48 hrs at  $-60^\circ\text{C}$ . After this time the reaction mixture was warmed to room temperature and the solvent removed *in vacuo*. The residue was dissolved in dry hexane and filtered through Celite®. The hexane was removed *in vacuo* and the oily residue was distilled ( $5 \times 10^{-2}$  mbar,  $50^\circ\text{C}$ ) into a liquid nitrogen cooled Schlenk yielding 1.90g (80%) of a red-orange oil.



Analysis for compound made by both method was identical. Found C 62.36%, H 6.69%, Calc.: C 62.51%, H 6.82%.  $^1\text{H}$  NMR (300.22 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : -0.39 (dd, 1H,  $\underline{\text{CH}}$ ,  $^3\text{J} = 9.2\text{Hz}$ ,  $^2\text{J} = 1.5\text{Hz}$ ), -0.27 (d, 1H,  $^2\text{J} = 1.6\text{ Hz}$ ,  $\underline{\text{CH}}$ ), 1.77 (dd, 1H,  $\underline{\text{CH}}$ ,  $^3\text{J} = 6.5\text{Hz}$ ,  $^2\text{J} = 1.5\text{Hz}$ ), 1.89 (d, 1H,  $\underline{\text{CH}}$ ), 2.05 (s, 3H, Me), 4.63 (s, 5H,  $\eta^5\text{-Cp}$ ), 4.93 (dd, 1H,  $\underline{\text{CH}}$ ,  $^3\text{J} = 9.2\text{Hz}$ ,  $^3\text{J} = 6.5\text{Hz}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.50 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 23.8 ( $\underline{\text{CH}_3}$ ), 30.7( $\underline{\text{CH}_2}$ ), 34.4 ( $\underline{\text{CH}_2}$ ), 79.0 ( $\underline{\text{CH}}$ ), 80.6 ( $\text{C}_5\text{H}_5$ ), 94.6 ( $\underline{\text{C-Me}}$ ).

Complexes **2**, **3**, **4**, **5** and **6** were prepared using both method A and B. Complexes **6**, **7**, **8**, **9**, **10** and **11** were synthesized using methodology A.

**Synthesis of 2:** Complex **2** was prepared using both method A and B in an analogous fashion to that of **1** with the exception of the addition of 2,3-dimethyl butadiene (Method A: 0.85 mL, 7.5 mmol, Method B 1.7ml, 15 mmol) in place of isoprene. Sublimation ( $5 \times 10^{-2}$  mbar,  $60^\circ\text{C}$ ) of the residue yielded red-orange crystals. Method A: 0.66g (64%), Method B: 1.42g (69%). Analysis. Found C 63.97%, H 7.36%, Calc.: C 64.08%, H 7.33%.  $^1\text{H}$  NMR (300.22MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : -0.57 (d, 2H,  $\underline{\text{CH}}$ ,  $^2\text{J} = 0.9\text{ Hz}$ ), 1.66 (d, 2H,  $\underline{\text{CH}}$ ,  $^2\text{J} = 0.9\text{ Hz}$ ) 1.88 (s, 6H, Me), 4.43 (s, 5H,  $\eta^5\text{-Cp}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.50 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 20.7 ( $\underline{\text{CH}_3}$ ), 35.2 ( $=\underline{\text{CH}_2}$ ), 81.0 ( $\underline{\text{C}_5\text{H}_5}$ ), 91.8 ( $\underline{\text{C-Me}}$ ).

**Synthesis of 3:** Complex **3** was prepared using methods A and B in the presence of cyclopentadiene (0.63mL, 7.5mmol (Method A) or 1.26 ml, 15 mmol (method B)). Sublimation of **6** ( $5 \times 10^{-2}$  mbar,  $50^\circ\text{C}$ ) afforded a dark red solid. Method A: 0.68g (72%), Method B: 1.61g (85%). Analysis. Found C 63.12%, H 5.80%, Calc.: C 63.17%, H 5.83%.  $^1\text{H}$  NMR (300.22MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 2.02 (m, 1H,  $\underline{\text{CH}_2}$ ), 2.40 (m, 2H,  $\underline{\text{CH}}$ ), 2.56 (m, 1H,  $\underline{\text{CH}_2}$ ), 4.56 (s, 5H,  $\eta^5\text{-Cp}$ ), 5.23 (m, 2H,  $\underline{\text{CH}}$ ).  $^{13}\text{C}\{^1\text{H}\}$ c NMR (75.50 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 39.4 ( $\underline{\text{CH}_2}$ ), 41.7 ( $\underline{\text{CH}}$ ), 77.3 ( $\underline{\text{CH}}$ ), 79.8 ( $\underline{\text{C}_5\text{H}_5}$ ).

**Synthesis of 4:** Complex **4** was synthesized using both method A, in the presence of 0.72 mL (7.5 mmol) of 1,3-cyclohexadiene, and Method B in the presence of 1.43 mL (15 mmol) of 1,3-cyclohexadiene. Sublimation ( $5 \times 10^{-2}$  mbar,  $60^\circ\text{C}$ ) yielded a red-orange solid. Method A: 0.66g (65%), Method B: 1.45g (71%). Analysis. Found C 64.76%, H 6.48%, Calc.: C 64.71%, H 6.42%.  $^1\text{H}$  NMR (300.22MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 0.77 (d, 2H,  $\underline{\text{CH}_2}$ ), 1.43 (m, 2H,  $\underline{\text{CH}_2}$ ), 2.91 (m, 2H,  $\underline{\text{CH}}$ ), 4.50 (s,

5H,  $\eta^5$ -Cp), 4.71 (m, 2H, CH). Identification was confirmed by a comparison of the spectroscopic data with literature.

**Synthesis of 5:** Complex **5** was synthesized using both Method A, in the presence of 0.76 mL (7.5mmol) of, norbornadiene, and Method B in the presence of 1.53 mL (15 mmol) of norbornadiene. Recrystallization of **5** from a saturated hexane solution at  $-28^\circ\text{C}$  afforded dark brown-orange crystals. Method A: 0.76g (69%), Method B: 1.56g (72%). **5** could be further purified by sublimation ( $5 \times 10^{-2}$  mbar,  $80^\circ\text{C}$ ). Analysis. Found C 66.74%, H 6.09%, Calc.: C 66.68%, H 6.06%.  $^1\text{H}$  NMR (250.13MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 0.78 (m, 2H, CH<sub>2</sub>), 2.70 (m, 4H, CH), 3.03 (m, 2H, CH), 4.42 (s, 5H,  $\eta^5$ -Cp). Identification was confirmed by a comparison of the spectroscopic data with literature.

**Synthesis of 6:** Complex **6** was synthesized using both Method A, in the presence of 0.92 mL (7.5mmol) of, 1,5-cyclooctadiene, and Method B in the presence of 1.84 mL (15 mmol) of 1,5-cyclooctadiene. Recrystallization of **6** from a saturated hexane solution at  $-28^\circ\text{C}$  afforded yellow-orange crystals. Method A: 0.84g (72%), Method B: 1.63g (70%). Analysis. Found C 67.09%, H 7.47%, Calc.: C 67.24%, H 7.38%.  $^1\text{H}$  NMR (250.13MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 1.79 (m, 4H, CH), 2.56 (m, 4H, CH<sub>2</sub>), 3.55 (m, 4H, CH<sub>2</sub>), 4.46 (s, 5H,  $\eta^5$ -Cp). Identification was confirmed by a comparison of the spectroscopic data with literature.

**Synthesis of 7:** Complex **7** was synthesized using method A using 0.44g of sodium methylcyclopentadienyl (5mmol) and 0.75 mL of Isoprene (7.5 mmol). Distillation ( $5 \times 10^{-2}$  mbar,  $50^\circ\text{C}$ ) yielded a 0.64 g of a red-orange liquid (62%). Analysis. Found C 63.84%, H 7.44%, Calc.: C 64.08%, H 7.33%.  $^1\text{H}$  NMR (300.22MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : -0.51 (dd, 1H, CH), -0.34 (d, 1H, CH), 1.62 (s, 3H,  $\eta^5$ -Cp-Me), 1.72 (dd, 1H, CH) 1.85 (d, 1H, CH), 2.01 (s, 3H, Me), 4.46 (t, 2H,  $\eta^5$ -Cp-H), 4.52 (t, 2H,  $\eta^5$ -Cp-H), 4.87 (dd, 1H, CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.50 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 13.9 (Cp-Me), 23.3 (C-CH<sub>3</sub>), 32.3 (CH<sub>2</sub>), 35.4 (CH<sub>2</sub>), 79.0 (CH), 79.9 (C<sub>4</sub>H<sub>4</sub>-Me), 81.7 (C<sub>4</sub>H<sub>4</sub>-Me), 93.9 (C<sub>ipso</sub>), 94.2 (C-Me).

**Synthesis of 8:** Complex **8** was prepared using method A with of the addition of sodium methylcyclopentadienyl (0.44g, 5mmol) and 0.85 mL (7.5 mmol) of 2,3-dimethylbutadiene. Distillation ( $5 \times 10^{-2}$  mbar,  $50^\circ\text{C}$ ) yielded 0.79 g of a red-orange liquid (72%). Analysis. Found C 65.59%, H 7.86%,

Calc.: C 65.45%, H 7.78%.  $^1\text{H}$  NMR (300.22MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : -0.40 (d, 2H,  $\underline{\text{CH}}$ ), 1.63 (br s, 5H, Cp- $\underline{\text{Me}}$  & 2 CH) 1.97 (s, 6H, Me), 4.41 (s, 2H,  $\eta^5\text{-Cp-}\underline{\text{H}}$ ), 4.52 (s, 2H,  $\eta^5\text{-Cp-}\underline{\text{H}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.50 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 13.6 (Cp- $\underline{\text{Me}}$ ), 20.2 (C- $\underline{\text{Me}}$ ), 36.3 ( $\underline{\text{CH}_2}$ ), 80.1 ( $\underline{\text{C}_4\text{H}_4\text{-Me}}$ ) 82.1, ( $\underline{\text{C}_4\text{H}_4\text{-Me}}$ ) 91.0 (C-Me), 93.8 ( $\underline{\text{C}_{\text{ipso}}}$ ).

Synthesis of **9**: Complex **9** was prepared using method A with of the addition of sodium methylcyclopentadienyl (0.44g, 5mmol) and 0.72 mL (7.5 mmol) of 1,3-cyclohexadiene. Distillation ( $5 \times 10^{-2}$  mbar,  $60^\circ\text{C}$ ) yielded 0.71g (69%) of a red-orange oil. Analysis. Found C 66.17%, H 7.12%, Calc.: C 66.06%, H 6.93%.  $^1\text{H}$  NMR (300.22MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 0.93 (m, 2H,  $\underline{\text{CH}_2}$ ), 1.56 (m, 2H,  $\underline{\text{CH}_2}$ ), 1.81 (s, 3H, Cp- $\underline{\text{Me}}$ ), 2.87 (m, 2H,  $\underline{\text{CH}}$ ), 4.40 (t, 2H,  $\eta^5\text{-Cp-}\underline{\text{H}}$ ), 4.57 (t, 2H,  $\eta^5\text{-Cp-}\underline{\text{H}}$ ), 4.79 (m, 2H,  $\underline{\text{CH}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.50 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 14.4 (Cp- $\underline{\text{Me}}$ ), 26.3 ( $\text{CH}_2$ ), 54.9 (CH), 78.0 (CH), 80.1 ( $\underline{\text{C}_4\text{H}_4\text{-Me}}$ ), 81.1 ( $\underline{\text{C}_4\text{H}_4\text{-Me}}$ ), 94.9 ( $\underline{\text{C}_{\text{ipso}}}$ ).

Synthesis of **10**: Complex **10** was prepared using method A with of the addition of sodium methylcyclopentadienyl (0.44g, 5mmol) and 0.76 mL (7.5mmol) of, norbornadiene. Distillation ( $5 \times 10^{-2}$  mbar,  $80^\circ\text{C}$ ) yielded 0.58g (50% yield) of brown-yellow oil. Analysis. Found C 67.97%, H 6.69%, Calc.: C 67.83%, H 6.57%.  $^1\text{H}$  NMR (250.13MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 0.89 (m, 2H,  $\underline{\text{CH}_2}$ ), 1.35 (s, 3H,  $\eta^5\text{-Cp-}\underline{\text{Me}}$ ), 2.63 (m, 4H,  $\underline{\text{CH}}$ ), 3.17 (m, 2H,  $\underline{\text{CH}}$ ), 4.22 (t, 2H,  $\eta^5\text{-Cp-}\underline{\text{H}}$ ), 4.83 (t, 2H,  $\eta^5\text{-Cp-}\underline{\text{H}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.50 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 12.8 (Cp- $\underline{\text{Me}}$ ), 26.3 ( $\text{CH}_2$ ), 55.6 (CH), 81.0 (CH), 82.2 ( $\underline{\text{C}_4\text{H}_4\text{-Me}}$ ), 84.1 ( $\underline{\text{C}_4\text{H}_4\text{-Me}}$ ), 93.9 ( $\underline{\text{C}_{\text{ipso}}}$ ).

Synthesis of **11**: Complex **11** was prepared using method A with of the addition of sodium methylcyclopentadienyl (0.44g, 5mmol) and 0.92 mL (7.5mmol) of, 1,5-cyclooctadiene. Complex **11** was isolated by distillation ( $5 \times 10^{-2}$  mbar,  $80^\circ\text{C}$ ) as 0.71g (58%) a yellow-brown oil. Analysis. Found C 68.41%, H 7.84%, Calc.: C 68.29%, H 7.78%.  $^1\text{H}$  NMR (250.13MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 1.40 (s, 3H,  $\eta^5\text{-Cp-}\underline{\text{Me}}$ ), 1.74 (dd, 4H,  $\underline{\text{CH}}$ ), 2.48 (m, 4H,  $\underline{\text{CH}_2}$ ), 3.29 (m, 4H,  $\underline{\text{CH}_2}$ ), 4.15 (t, 2H,  $\eta^5\text{-Cp-}\underline{\text{H}}$ ), 4.47 (t, 2H,  $\eta^5\text{-Cp-}\underline{\text{H}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.50 MHz,  $\text{C}_6\text{D}_6$ , 298K)  $\delta$ : 12.9 (Cp- $\underline{\text{Me}}$ ), 32.9 ( $\text{CH}_2$ ), 83.6 (CH), 84.0 ( $\underline{\text{C}_4\text{H}_4\text{-Me}}$ ), 85.6 ( $\underline{\text{C}_4\text{H}_4\text{-Me}}$ ), 96.0 ( $\underline{\text{C}_{\text{ipso}}}$ ).

## Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarized in Table 1S (see the SI). For both structures, data was collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Structure solution and refinements were performed using SHELX86<sup>41</sup> and SHELX97<sup>42</sup> software, respectively. Corrections for absorption were made in all cases. Data was processed using the Nonius Software.<sup>43</sup> Structure solution, followed by full-matrix least squares refinement was performed using the WINGX-1.80 suite of programs throughout.<sup>44</sup> For all complexes, hydrogen atoms were included at calculated positions. Data for complexes **2**, **5** and **6** are deposited with the Cambridge Structural Database with CCDC reference numbers 1477351-1477353.

## Materials Chemistry

TGA Analysis of the complexes was performed at SAFC Hitech, Bromborough, UK, using a Shimadzu TGA-51 Thermogravimetric Analyzer. Data points were collected every second at a ramp rate of 5 °C min<sup>-1</sup> in a flowing (50 mL min<sup>-1</sup>) N<sub>2</sub> stream. Isothermal TGAs were run at 73 °C in a flowing (10 mL min<sup>-1</sup>) N<sub>2</sub> stream, with run times of 12 mins 28 mins and 107 mins, for complexes **1**, **2** and **4**, respectively. Thin films were deposited using a modified cold-walled CVD system (ElectroGas Systems Ltd, UK). The system consisted of a tubular quartz reactor containing a silicon carbide coated graphite susceptor. The temperature of the susceptor was monitored using a k-type thermocouple coupled with a proportional–integral–derivative controller (PID controller), and heated with a water cooled IR lamp mounted externally beneath the reaction tube. The pressure of the system was maintained at 760 Torr throughout the deposition run, with the reactor lines and precursor, held in a bubbler, at 90 and 85 °C respectively. The vapor generated was delivered to the reaction zone using a high purity Hydrogen (99.998%) carrier gas (300 mL min<sup>-1</sup>) metered from a mass flow controller. Films were deposited onto CVD coated ruthenium on silicon wafers at a susceptor temperature of between 325-400 °C. The total deposition time per sample was 30 min.

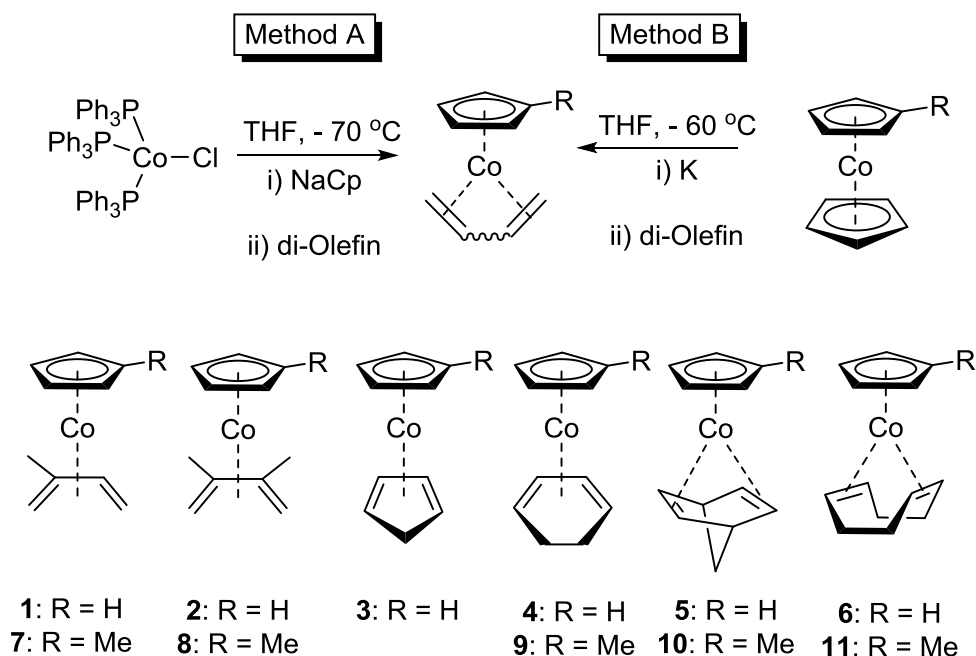
Raman spectroscopy was recorded on a Renishaw *InVia* Raman using a 532 nm (green) laser. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra-DLD photoelectron spectrometer, utilizing monochromatic Al K<sub>α</sub> radiation (photon energy 1486.6 eV), at the University of Cardiff. The instrument was pre-calibrated using pure gold and copper samples. Samples were sputtered for a pre-determined set time over a 4 mm wide area using 4 kV argon ions using a minibeam I ion source. Spectra were collected at pass energies of 80 and 160 eV for high resolution and survey scans respectively, with the 100 μm aperture in place to focus on the centre of the etch pit. FE-SEM analysis of the films was undertaken on a JEOL JSM-6480LV scanning electron microscope with EDX capability. AFM analysis was performed using a Digital Instruments Nanoscope IIIa, with TAP300 tips in contact mode (Tip radius <10nm). Powder XRD of the films was performed on a Bruker D8 Powder Diffractometer, using a Cu anode X-ray source, (K<sub>α</sub> wavelength = 1.5406 Å) at the University of Bath. Sheet resistance measurements were recorded using a Jandel

Multi-height 4-point probe in combination with a Guardian Surface Resistance Meter Model #SRM-232-100, with a sheet resistance range of 0-100 ohm/sq.

## Results and Discussion

### Synthesis

The cobalt di-olefin complexes **1-11** can be easily prepared by a number of synthetic routes,<sup>34-35,40,45</sup> however focus was given to two specific methods (Scheme 1) which could easily scaled to provide larger quantities of precursor from equally scalable starting materials.



**Scheme 1:** Synthetic Methods A and B.

While complexes **1-11** were initially prepared by the reaction of  $\text{ClCo}(\text{PPh}_3)_3$  with NaCp, followed by a thermally driven substitution of  $\text{PPh}_3$  with the appropriate di-olefin ligand (Method A: Scheme 1), products were invariably contaminated with triphenylphosphine, which could be successfully removed by either careful sublimation or crystallization of the product. For this reason, an alternative large scale preparative method of production was sought: Using a modification of the procedure used to produce the Jonas reagent,  $[\text{CpCo}(\text{H}_2\text{C}=\text{CH}_2)_2]$ ,<sup>34</sup> we were able to synthesis complexes **1-6** in high yield without the need utilize the gaseous reagent ethene or trimethylsilylethene<sup>35</sup> (Method B: Scheme 1).

However, because difficulties encountered in the large scale production of *bis*-methyl-cyclopentadienyl cobalt (dimethyl-cobaltocene) complexes **7-11** were produced, exclusively, using method A and sodium methyl-cyclopentadienide (NaCpMe).

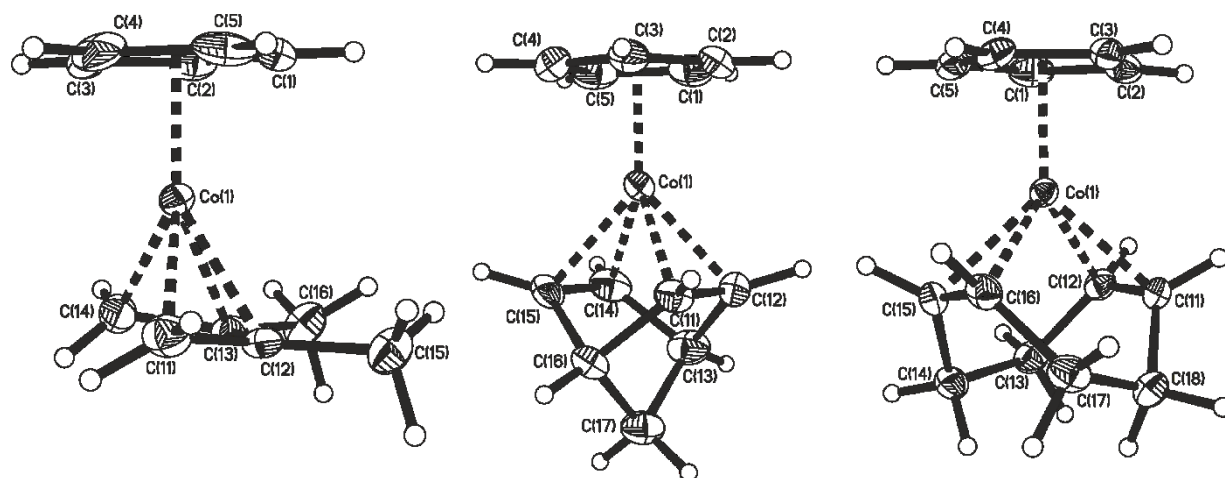
Room temperature  $^1\text{H}$  NMR of complexes **1-6** showed all of the complexes to be diamagnetic, indicative of a cobalt(I) environment, and to possess characteristic singlet resonances for  $\eta^5\text{-Cp-H}$  between  $\delta = 4.4$  and  $4.7$  ppm; The  $^1\text{H}$  NMR spectra of complexes **1** and **2** show the expected methyl [**1**: 2.05 ppm; **2**: 1.88 ppm] and olefinic protons [**1**: -0.27, -0.39, 1.77, 1.89, 4.93 ppm; **2**: -0.5, 1.66 ppm]. The  $^1\text{H}$  NMR spectra for complexes **3-6** show the presence of the expected olefinic protons [**3**: 2.40, 5.23 ppm; **4**: 2.91, 4.50 ppm; **5**: 2.70 ppm; **6**: 1.79 ppm ] as well as the methene ( $\text{CH}_2$ ) protons [**3**: 2.02, 2.56 ppm; **4**: 0.77, 1.43 ppm; **5**: 0.78 ppm; **6**: 2.56, 3.55 ppm].

The  $^1\text{H}$  NMR spectra for the complexes **7-11** are similar to the related complexes, **1-2** and **4-6**, with respect to the resonances di-olefin ligand. Each  $^1\text{H}$  NMR spectra also contain a multiplet resonance between  $\delta = 4.15 - 4.83$  ppm for the  $\text{C}_5\text{H}_4\text{-Me}$  hydrogens, which correlate to resonances between  $\delta = 79.9 - 85.6$  (for the  $\{\text{C}_4\text{H}_4\text{CMe}\}$  carbon atoms) and  $93.8 - 96.0$  ppm ( $\text{C}_{\text{ipso}}$ ), respectively, for the three distinct carbon atoms in the  $\{\eta^5\text{-C}_5\text{H}_4\text{-Me}\}$  rings in the associated  $^{13}\text{C}$  NMR spectra.

### ***Molecular structures of 2, 5 and 6***

Of the eleven complexes reported in this study, single crystals suitable for single crystal X-ray diffraction studies of only three complexes, **2**, **5** and **6**, could be isolated; In the case of **2** slow sublimation onto a water cooled cold finger ( $1^\circ\text{C}$ ) yielded crystals suitable for X-ray studies. In the case of **5** and **6** crystals were grown from saturated hexane solutions at  $-28^\circ\text{C}$ . All three complexes were characterized by single crystal X-ray diffraction to unambiguously determine the solid state molecular structures of the products and are relatively rare examples of  $\text{CpCo(I)}$  complexes with di-olefin ligands. Experimental crystallographic data are summarized in the SI, the molecular structures

of the complexes are shown in Figure 1, and selected bond lengths and angles for **2**, **5** and **6** are shown in Table 1.



**Figure 1** Molecular structures of **2** (left), **5** (middle) and **6** (right) in the solid state. Thermal ellipsoids are shown at 50% probability.

In the solid state complexes **2**, **5** and **6** all adopt mononuclear structures, in which the metal centers possess a *pseudo*-trigonal-planar environment, which comprises of the  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> ligand and the two alkene moieties. Crystallizing in the monoclinic space group P2<sub>1</sub>/c with one molecule in the asymmetric unit, the overall structure of **2** is as expected with the 2,3-dimethylbutadiene molecule bound in an  $\eta^4$ -fashion via the double bonds to a {CpCo} group, in an analogous fashion to the related rhodium complex [CpRh( $\eta^4$ -CH<sub>2</sub>C(Me)C(Me)CH<sub>2</sub>)].<sup>46</sup> The molecule itself possesses a pseudo mirror plane bisecting both the cyclopentadienyl and dimethyl-butadiene ligands (through atom C(1) and the mid-points of the C(2)-C(3) and C(12)-C(13) bond). The C(1) end of the {Cp} ring is tilted away from the plane of the butadiene ligand [C(11)-C(12)-C(13)-C(14)] such that the two planes intersect at a small angle of 9.3°. The cobalt center is 1.68 Å and 1.57 Å from the {Cp<sub>cent</sub>} and {C<sub>4</sub>} planes respectively.

Examination of the 1,3-diene moiety shows a uniform range of C-C bond lengths [1.43 Å, 1.44 Å and 1.43 Å for the formal C(11)=C(12), C(12)-C(13) and C(13)=C(14)] indicative of an effective Co  $\rightarrow$ 1,3-diene  $\pi$ -electron density back donation, where the double single-double bond alterations



observed in free 2,3-dimethylbutadiene are transformed into delocalized bonds intermediate between C=C and C-C bonds. As a result charge separation between the cobalt central atom and the ligands are somewhat minimized, resulting in a relatively non-polar bonding situation.

**Table 1:** Selected bond lengths and angles for **2**, **5** and **6**

	<b>Bond Distances (Å)</b>		
	<b>2</b>	<b>5*</b>	<b>6</b>
Co-( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>(cent)</sub>	1.68	1.70	1.71
Co(1)-C(11)	2.024	2.005	2.021
Co(1)-C(12)	1.983	1.999	2.014
Co(1)-C(13)	1.985	-	-
Co(1)-C(14)	2.022	2.012	
Co(1)-C(15)	-	2.014	2.026
Co(1)-C(16)	-	-	2.016
C(11)-C(12)	1.432	1.410	1.415
C(12)-C(13)	1.437	-	-
C(13)-C(14)	1.429	-	-
C(14)-C(15)	-	1.407	-
C(15)-C(16)	-	-	1.414
	<b>Bond Angles (°)</b>		
Cp <sub>cent</sub> -Co- $\{C=C\}^a$	145.20	142.89	134.49
	147.00	141.83	133.86
$\{C=C\}^a$ -Co- $\{C=C\}^a$	66.31	75.28	91.65
C(11)-C(12)-C(13)	115.29	-	-
C(12)-C(13)-C(14)	115.18	-	-
C(11)-C(12)-C(13)-C(14)	0.3	-	-
C(11)-C(12)-C(14)-C(15)	-	0.1	-
C(11)-C(12)-C(15)-C(16)	-	-	8.8

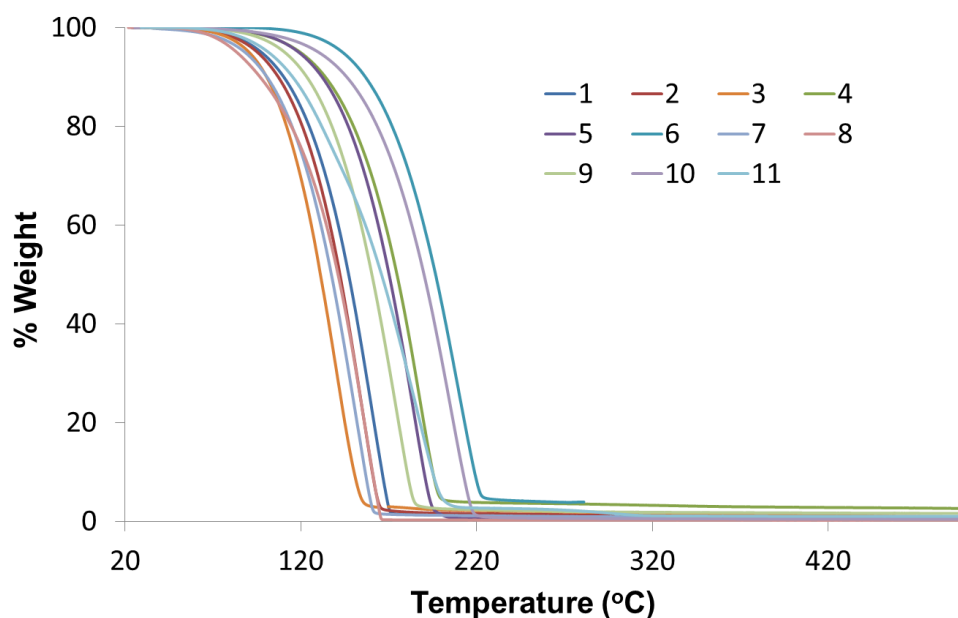
\*: data for only one of the two molecules in the asymmetric unit is reported for **5**; <sup>a</sup>: mid-point of the C=C bonds.

Complexes **5** and **6** are similarly mononuclear structures, in which the metal centers possess a *pseudo*-trigonal-planar environment, with the conjugated diene ligand replaced by the non-conjugated diene ligands, norbornadiene (NBD) and 1,5-cyclooctadiene (COD). The norbornadiene derivative **5** crystallizes in the monoclinic space group C2/c with two molecules in the asymmetric unit, with rotational disorder within the {C<sub>5</sub>H<sub>5</sub>} ligand based on one of the two molecules of **5** (Co(2)). In contrast complex **6** crystallizes in the space group P2<sub>1</sub>/c with one molecule in the asymmetric unit. The Cp-Co interactions in **5** and **6** are comparable to that observed in complex **2** [**2**: Co-C(ave) = 2.065 Å, Co-Cp(cent) = 1.68 Å; **5**: Co-C(ave) = 2.081 Å, Co-Cp(cent) = 1.70 Å; **6**: Co-C(ave) = 2.093 Å, Co-Cp(cent) = 1.71 Å] and is in the expected range. As anticipated, coordination of the electron rich

olefin groups to the Co(I) metal center results in some lengthening of the olefin bond [**5**: C(11)-C(12) = 1.41 Å, C(14)-C(15) = 1.41; **6**: C(11)-C(12) = 1.42, C(15)-C(16) = 1.42 Å] and a loss of some double bond character [ $d_{\text{NBD}}(\text{C}=\text{C}) = 1.34 \text{ \AA}$ ].

## ***Thermal Profile of Complexes and use as Deposition Precursor***

Thermogravimetric analysis (TGA) of complexes **1-11** were performed in order to gain insight into relative volatilities and thermal stabilities. These analysis was carried out with an instrument that was housed in a nitrogen filled purge-box in order to minimize reaction with atmospheric moisture/air. Figure 2 shows TGA plots for complexes **1-11** and Table 2 summarises the TGA data for **1-11**. All compounds were found to undergo mass loss and yield a stable residue of 3.7-0.3 % at a temperature between 165-310 °C, respectively. All final mass values are significantly below the expected values for cobalt for all complexes, indicating that volatilisation has occurred with minimal thermal decomposition. Thermal stability at volatilisation temperatures is an important physical property as it ensures consistent precursor doses and therefore consistent film thicknesses from run to run.



**Figure 2:** Thermogravimetric analysis traces of **1-11** from 20 to 500 °C. Experiments were run under N<sub>2</sub> (50 mL min<sup>-1</sup>) at a ramp rate of 5 °C min<sup>-1</sup>.

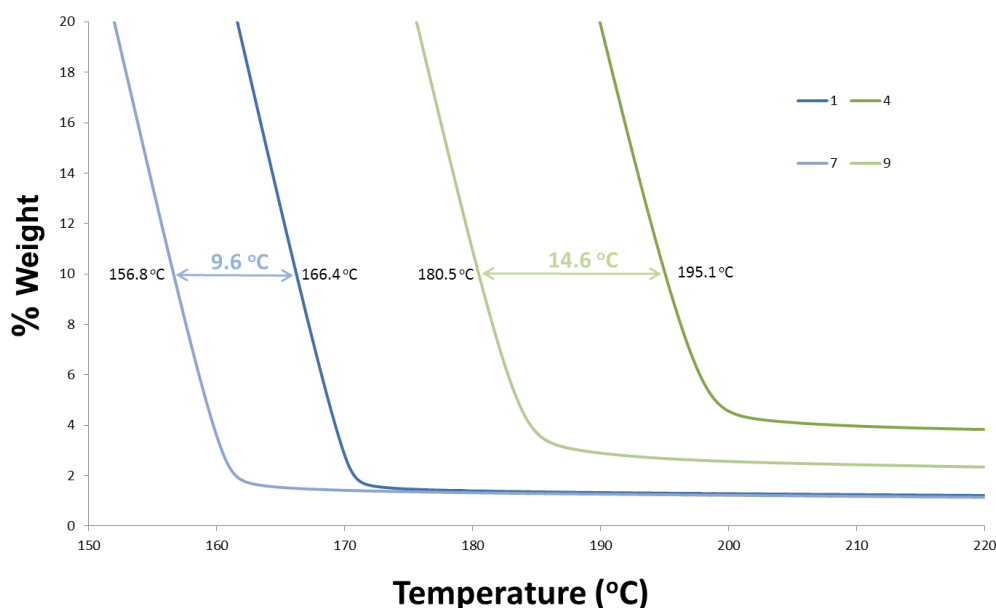
**Table 2:** Expected % residue, % of non-volatile residue and onset of volatilisation/decomposition temperature for **1-11**.

Precursor	Expected % for Co	% Non-volatile Residue (Temp.)	Onset Temp. <sup>§</sup>
<b>1</b>	30.7	1.2 (225 °C)	73 °C
<b>2</b>	28.6	1.7 (195 °C)	73 °C
<b>3</b>	31.0	2.8 (165 °C)	70 °C
<b>4</b>	28.9	3.7 (240 °C)	92 °C
<b>5</b>	27.3	2.8 (216 °C)	93 °C
<b>6</b>	25.4	3.8 (270 °C)	119 °C
<b>7</b>	28.6	1.2 (200 °C)	62 °C
<b>8</b>	26.8	0.3 (168 °C)	64 °C
<b>9</b>	27.0	2.4 (212 °C)	86 °C
<b>10</b>	23.6	0.5 (310 °C)	95 °C
<b>11</b>	23.9	2.6 (230 °C)	77 °C

<sup>§</sup> The temperature at which 1% mass loss has occurred

We have previously investigated the relationship between alkyl group functionalization of the cyclopentadienyl ligand, and both volatility and stability in copper cyclopentadienide isocyanate complexes<sup>47</sup>: If we compare the temperatures at which the onset of volatilization is observed for the ten compounds for which both the cyclopentadienyl and methyl cyclopentadienyl complex has been synthesised, the general trend appears to be that the addition of a methyl substituent onto the {Cp} fragment results in a lowering of the temperature at which mass loss begins [**1**(73 °C):**7**(62 °C); **2**(73 °C):**8**(64 °C); **4**(92 °C):**9**(86 °C); **6**(119 °C):**11**(77 °C)]. This effect can clearly be seen in Figure 3, which shows a close-up of the TGA plots for the compounds **1-7** and **4-9** respectively: incorporation of asymmetry into the {Cp} fragment (i.e. a methyl group), results in a noticeable decrease in the temperature at which a mass loss occurs [ $\Delta_T = 9.6$  °C (**1-7**);  $\Delta_T = 14.6$  °C (**4-9**)]. It should be noted that the addition of a methyl substituent onto the {Cp} fragment can also lead to an increase in temperature

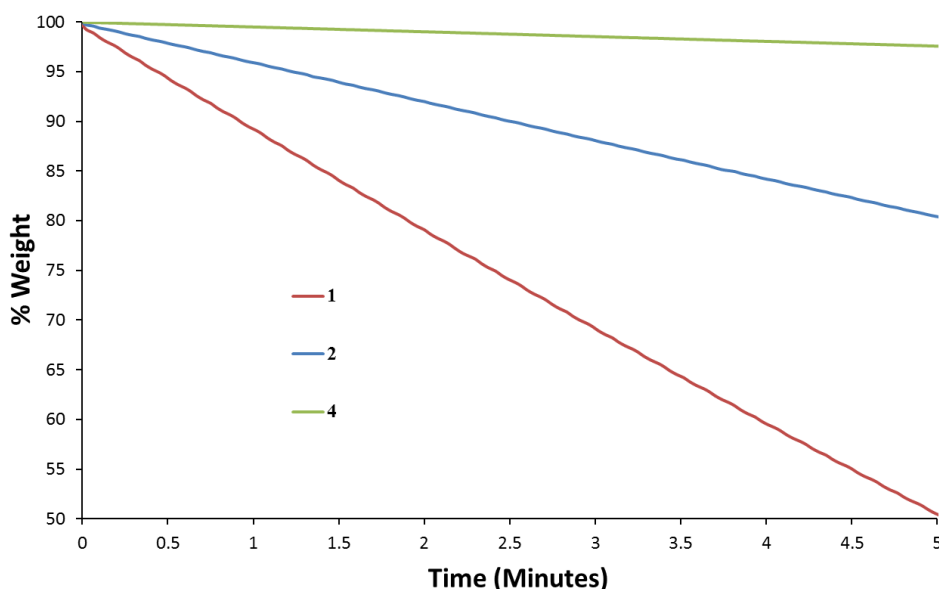
at which the onset of mass loss commences, specifically in the cases of compounds **5** (93 °C) and **10** (95 °C).



**Figure 3:** Comparison of the TGA traces of related complexes **1 & 7** and **4 & 9**.

The thermal stability of complexes **1-11** were studied by placing the neat compound inside an NMR tube containing a sealed capillary tube of  $C_6D_6$ . The  $^1H$  NMR spectra were recorded periodically (every 4 hrs) with the NMR tubes held at 75 °C in an oil bath between recording their NMR spectra. The degree of compound decomposition was estimated by comparison of the integrated areas under the {Cp-H}\_(or {MeCp}) NMR peak(s), and normalized to the residual protio solvent in the  $C_6D_6$  capillary. Interestingly compounds **1, 2, 4, 5** and **6** all showed relatively high thermal stabilities: in the case of complexes **1, 2** and **4** only minimal decomposition after 7 days (6 %, 2 % and 4% respectively) was observed, indicating a high thermal stability. For complexes **5** and **6** the presence of paramagnetic species in the NMR sample prohibited further monitoring after 3 to 4 days. However, compound **3** showed rather rapid thermal decomposition with formation of a metallic mirror on the inside of the NMR tube after only 6 hrs. Despite being liquids/oils and as such potentially useful as precursors, compounds **7-11** all showed significant decomposition and production of a metallic mirror on the NMR tube after 24-48 hours, indicating a significantly reduced thermal stability for the methyl derivatized complexes.

The liquid and semi solid complex **1**, **2** and **4**, all of which showed good thermal stability and were capable of being sublimed were further analyzed by isothermal gravimetric analysis (IT-TGA). Figure 4 shows an IT-TGA plot at 73 °C of compounds **1**, **2** and **4**. The plot shows all precursors to undergo mass loss at a constant rate. It also shows the order of volatility to be **1** > **2** > **4**, the former evaporating to 50 % of the starting mass within just 5 minutes, over twice the rate of the latter two.

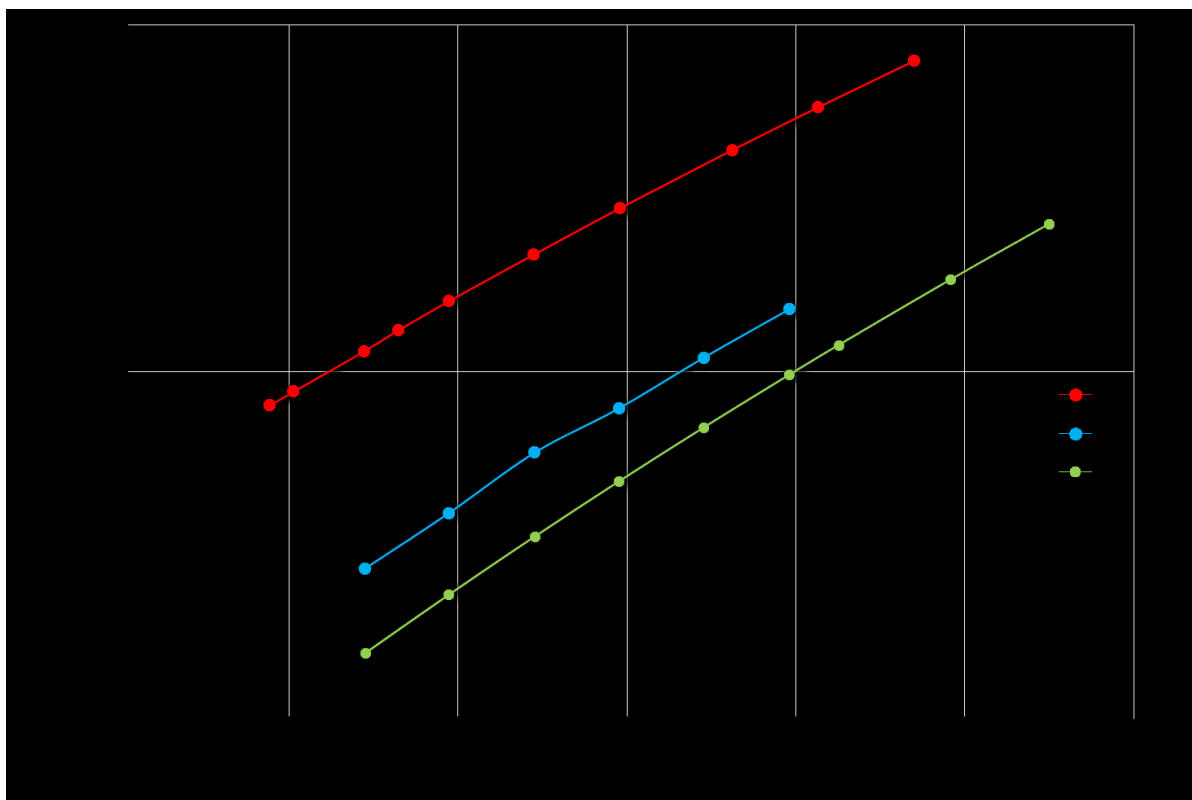


**Figure 4:** Isothermal - Thermogravimetric analysis (IT-TGA) traces of **1**, **2** and **4** at 73 °C (5 mins); IT-TGA for compounds **1**, **2** and **4** run for a total of 12 mins, 28 mins and 107 mins respectively.

Experiments were run under N<sub>2</sub> (10 mL min<sup>-1</sup>).

As part of our study, vapor pressure measurements were carried out on **1**, **2** and **4** using a previously reported method and apparatus.<sup>47,48</sup> Details of these analyses are supplied in the supporting information. The results of the vapor pressure measurements of **1**, **2** and **4** are depicted in Figure 5 and the numerical results shown in Table 3.

Each set of data was obtained at temperatures below the decomposition points of the precursors. The vapor pressures of **1**, **2** and **4** obey the general equation  $\log P = A - B/T$  : where A and B are free parameters, with the corresponding enthalpy of vaporization being deduced from the parameter B (Table 3).



**Figure 5.** Vapor pressure data for complexes **1**, **2** and **4**.

**Table 3.** Vapor pressure data for the precursors **1**, **2** and **4**. Data sets are fitted to  $\log P$  (mTorr) =  $A - (B)/(T/K)$ . Error margins are established by a linear regression method and given at the 95% confidence interval.

	<i>A</i>	<i>B</i>	$\Delta H_{\text{sub}}$ [kJ mol <sup>-1</sup> ]	Temp. range of measurement [°C]	Calc. vapor pressure @ 85 °C (Torr)
<b>1</b>	11.37 ± 0.04	26.79 ± 0.14	22.27 ± 0.12	28-67	7.83
<b>2</b>	11.89 ± 0.14	30.32 ± 0.44	25.21 ± 0.37	33-60	2.69
<b>4</b>	12.42 ± 0.04	32.70 ± 0.13	27.19 ± 0.11	33-75	1.95

Data shows that by far the most volatile of the complexes studied here is **1**, with a vapor pressure of 7.83 Torr at 85 °C. The vapor pressures recorded in Table 3 are all higher than those previously described cobalt-CVD precursors including cobaltocene,  $[(C_5H_5)_2Co]$ ,<sup>49</sup> the cobalt amidinate,  $[Co(tBuNC(Et)NEt)_2]$ ,<sup>25</sup> and the trimethylsilyl substituted systems  $[Co_2(CO)_6(\eta^2-Me_3SiC\equiv CR)]$  (R = SiMe<sub>3</sub>, H or n-C<sub>3</sub>H<sub>7</sub>)<sup>23</sup>, although notably significantly lower than both Co<sub>2</sub>(CO)<sub>9</sub> and alkyl systems  $[Co_2(CO)_6(\eta^2-RC\equiv CR)]$  (R = n-C<sub>3</sub>H<sub>7</sub> to n-C<sub>7</sub>H<sub>15</sub>).<sup>23b</sup>

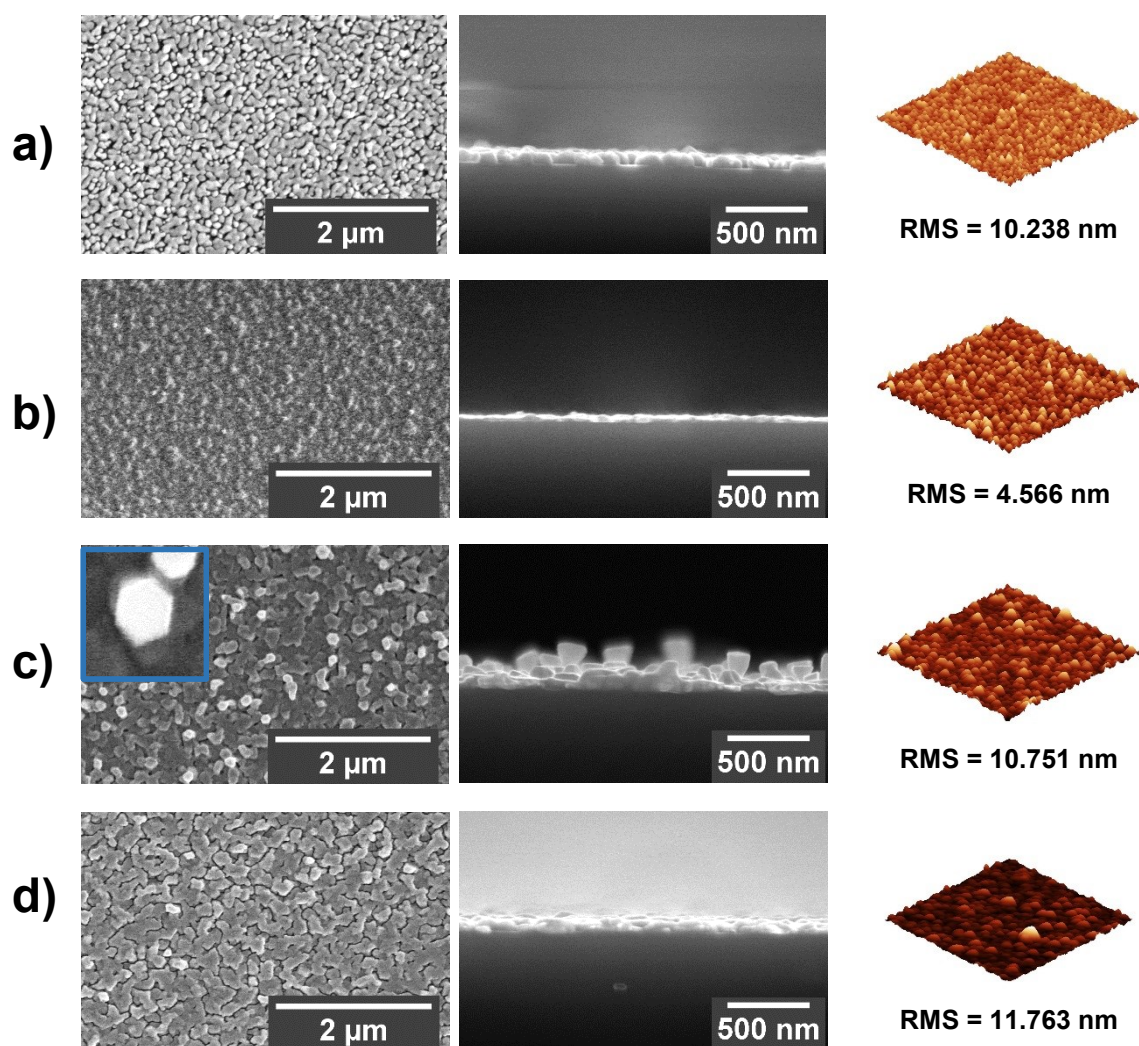
Resultantly, compound **1** was chosen as a good candidate for AP-MOCVD experiments owing to its attractive TGA profile, high vapor pressure and thermal stability. CVD experiments were performed in-house on a modified ElectroGas hot-walled reactor utilizing H<sub>2</sub> as a reducing gas. Substrates were silicon (100) wafers, pre-cleaned by washing with *aqua regia*, water and isopropanol and dried under a nitrogen flow. Table 4 summarizes the deposition conditions for complex **1**. The deposition of cobalt metal was investigated at four different substrate temperatures; 325 °C, 350 °C, 375 °C and 400 °C respectively. In all of the deposition runs the precursor and the carrier gas lines were externally heated to 130°C, and the pressure during deposition was maintained at 760 Torr. H<sub>2</sub> gas was used as the carrier gas at a flow rate of flow of 0.3 L min<sup>-1</sup>. Table 4 shows the general physical parameters used throughout the deposition experiments.

**Table 4:** Experimental conditions used for cobalt deposition from **1**.

Variable	Value
Temperature of Substrate	325, 350, 375 and 400°C
Bubbler temperature	85 °C
Path temperature	90 °C
Bulk flow rate (gas)	0.7 L/min (H <sub>2</sub> )
Flow rate over bubbler (gas)	0.3L/min (H <sub>2</sub> )
Pressure	760 Torr
Deposition time	30 minutes

Films deposited at 325 °C and 350 °C appeared reflective, metallic and continuous to the naked eye whereas films deposited at 375 and 400 °C, while also appearing reflective, metallic and continuous also showed some brown discoloration. At temperatures below 325 °C deposited films were powdery grey/blue and appeared discontinuous.

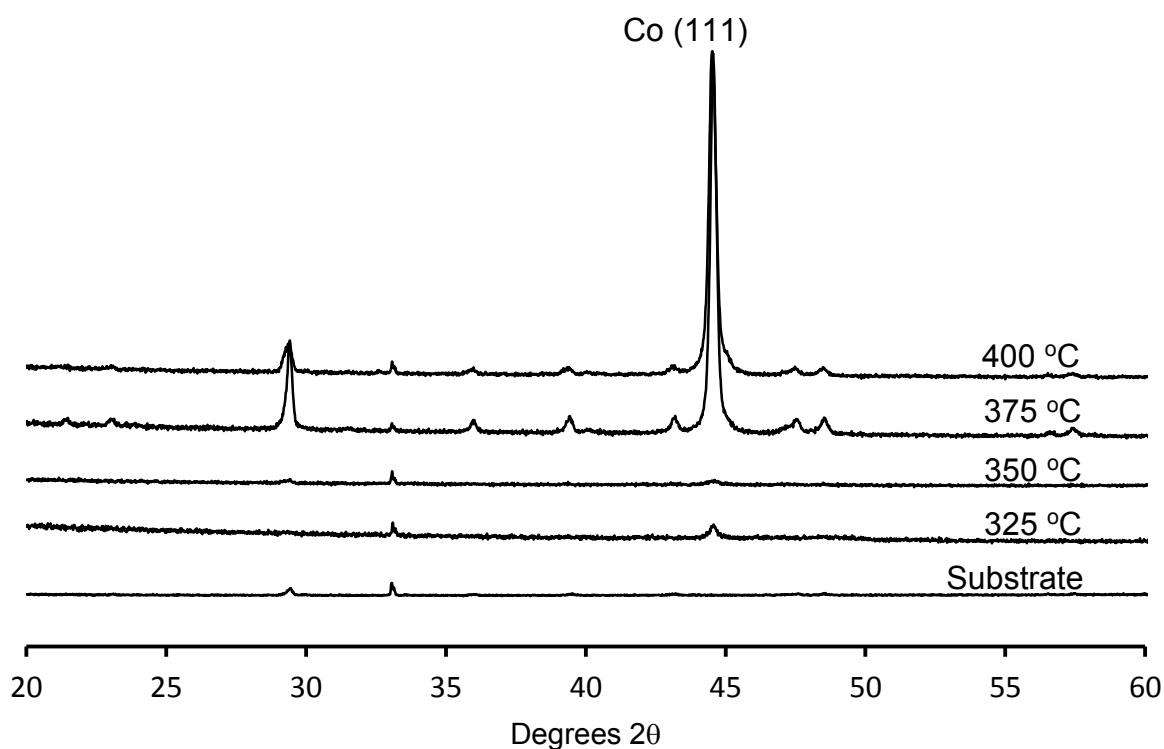
SEM and AFM micrographs of films grown from **1** are shown in Figure 7. SEM and AFM analysis showed the film morphology and film thickness to be dependent on temperature and, in general, particle sizes were found to increase with increasing deposition temperature which is in agreement with previous studies reported by Ivanova *et al*<sup>50</sup> and general thin film growth.



**Figure 7:** Top-down SEM (scale: 1 μm), cross-sectional SEM (x25,000 magnification) and AFM (5μm x 5μm) micrographs for films deposited at a substrate temperature of a) 325 °C, b) 350 °C, c) 375 °C and d) 400 °C.



Films deposited at 375 °C exhibit a high degree of crystallinity, with hexagonal particles clearly visible in the electron micrograph (inset Figure 7c). Films deposited at 325, 350 and 400 °C demonstrated excellent thickness uniformity, whereas films deposited at 375 °C appeared more uneven (RMS from AFM = 10.751 nm). All deposited films were analysed by XRD in order to ascertain the crystallographic orientation of the films (Figure 8). XRD of all films demonstrates crystal growth to be highly selective, resulting in the detection of only one single reflection at  $2\theta = 44.5^\circ$ , corresponding the (111) Miller plane associated with face centred cubic (fcc) cobalt metal; all other reflections can be associated with the silicon substrate. There is precedence in the literature for the preferential deposition of (111) fcc cobalt onto borosilicate glass.<sup>17c,51</sup>



**Figure 8:** XRD patterns of cobalt thin films deposited between 325-400 °C clearly showing the strong reflection from the Co (111) miller plane. The PXRD pattern of the (100) silicon substrate is also shown.

Deposition temperature clearly has an effect on the crystallinity of the films, and in general, the intensity of the (111) reflection increases with increasing temperature; the most intense (111) reflection was associated with thin films deposited at a substrate temperature of 375 °C, which is in

agreement with SEM data. The least intense (111) reflection was associated with films deposited at a substrate temperature of 350 °C, which is likely to be a consequence of the relative thinness of the film, as indicated by SEM analysis. The average crystallite sizes were calculated to be 88.4 nm (375 °C) and 73.4 nm (400 °C) using the Scherrer equation;<sup>52</sup> these values are in agreement with SEM data. Accurate calculations for films deposited at 325 °C and 350 °C were unobtainable due to weak diffraction.

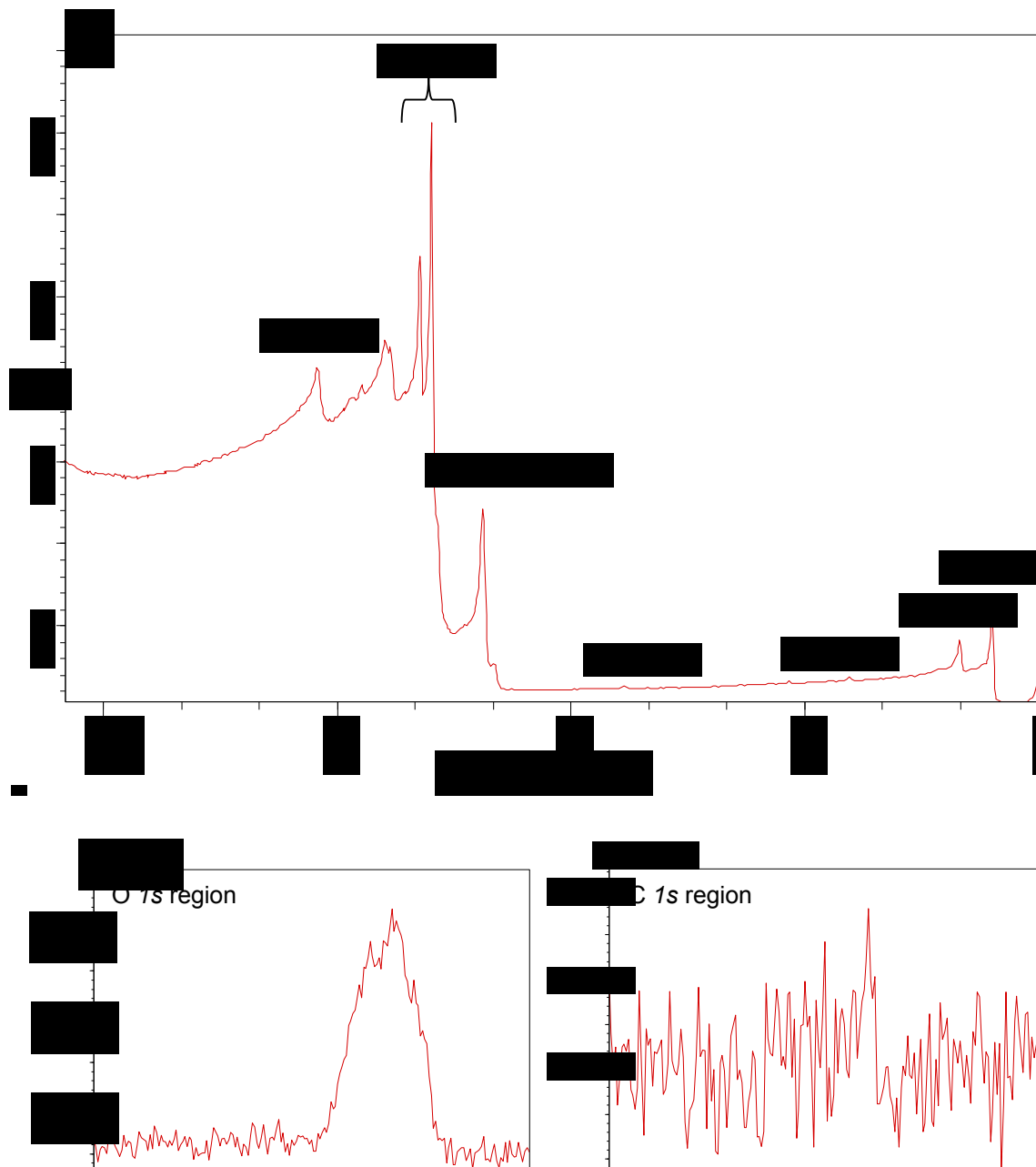
Film composition was studied by XPS analysis in order to determine the elemental composition of the thin films. Analysis of as-deposited films demonstrated the presence of metallic cobalt but also the presence of oxygen and carbon, likely to come from adsorbed organic species and surface oxidation. After etching the surface for a period of five minutes with an argon sputter oxygen and carbon peaks reduced to trace levels and the peaks associated with metallic cobalt ( $2s = 926$  eV,  $2p = 779$  eV, LMM =  $716$  eV,  $3s = 101$  eV and  $3p = 60$  eV) increased in intensity. Table 5 shows the elemental profile of etched films as a function of deposition temperature; quantification of the film was conducted using a Shirley background by integrating the area under the peaks and taking into account the relative sensitivity factors of each element.

**Table 5:** Atomic % of elements in cobalt thin films deposited at between 325 °C and 400 °C post-Ar etching (15 s). \*Quantification was performed assuming zero contribution from the silicon substrate. Values are expressed as atomic percentages.

Substrate Temperature	At.% Co*	At.% O*
325 °C	96.8	3.2
350 °C <sup>†</sup>	-	-
375 °C	97.0	3.0
400 °C	99.7	0.3

Figure 9 shows an XPS spectrum for a sample produced at 400 °C showing the presence of photoelectron peaks associated with metallic cobalt and the  $1s$  regions for carbon (284 eV) and oxygen (532 eV), which are common contaminants in deposited cobalt films. Analysis indicates that in

general, purity increases with increasing substrate temperature. Films deposited at a substrate temperature of 400 °C exhibit the highest purity (99.7 %) with trace amounts of oxygen (0.3 %) and no carbon, this compares favourably to previous deposition experiments, which have shown  $\text{CpCo}(\text{CO})_2$  to deposit metallic cobalt films with oxygen and carbon impurities of 1.0 % and 1.2 % respectively <sup>14b</sup>. Considering the high solubility of carbon in cobalt <sup>53</sup> the fact that no carbon can be detected in the deposited films at temperatures between 325-400 °C is quite remarkable, and shows that the hydrogen carrier gas is effective in the hydrogenation of all ligands cleanly from the substrate surface during deposition. There are however, oxygen impurities present in all films and considering that the precursor contains no oxygen it is reasonable to assume that oxygen contamination is coming either from the gas source, a leak in the reactor or *ex-situ* contamination.



**Figure 9:** Survey XPS spectrum of a Co thin film deposited at a substrate temperature of 400 °C

(above), with the *1s* regions for oxygen (bottom left) and carbon (bottom right) highlighted.

In stark contrast to our studies Dormans *et al.*<sup>17c</sup> suggest that the growth of cobalt thin films using the precursor  $\text{CpCo}(\text{CO})_2$ , are significantly retarded in the presence of  $\text{H}_2$  gas resulting in thin films at any temperature that are heavily contaminated with carbon (~50 %), a feature attributed to a change in deposition mechanism from reduction to disproportionation. Similar observations have been made in the deposition of nickel thin films from nickelocene by Rhee *et al.*<sup>54</sup> and Brissonneau *et al.*<sup>55</sup>. It is also noteworthy that while Raman spectroscopy shows a single Raman band at  $520.9 \text{ cm}^{-1}$ , and PXRD analysis shows a number of weak reflections, both associated with the silicon substrate, there is no

evidence from our analysis (including XPS) of cobalt silicide systems (*i.e.* Co<sub>2</sub>Si, CoSi and CoSi<sub>2</sub>),<sup>17b,18b,56</sup> contaminating the thin films.

The calculated growth rates for films grown from precursor **1** at 325 °C, 350 °C, 375 °C and 400 °C, respectively, are shown in Table 6; the values comparing favourably with previous studies reported in the literature by Haycock *et al.* using CpCo(CO)<sub>2</sub><sup>14b,c</sup> (1.38-1.40 nm min<sup>-1</sup>), although there is a drop in growth rate at 350 °C which is unexplained. The highest growth rate (4.18 nm min<sup>-1</sup>) was reached at 375 °C and diminishes thereafter; possibly due to desorption of the precursor from the substrate, or precursor depletion on the reactor walls at elevated temperatures.<sup>14b</sup> In contrast films deposited at 350 °C show a diminished growth rate, possibly due to competition between hydrogen and precursor for surface sites at this temperature.<sup>57</sup>

**Table 6:** Average bulk resistivity ( $\rho$ ) and sheet resistance ( $R_s$ ) values for cobalt films deposited from **1**. The bulk resistivity of cobalt = 5.6  $\mu\Omega\text{cm}$  (at 0 °C)<sup>58</sup>.

Temperature	Film Thickness (nm) [Growth rate (nm min <sup>-1</sup> )	$R_s$ ( $\Omega/\square$ )	$\rho$ ( $\mu\Omega\text{cm}$ )
325	79.5 [2.65]	4.05	32.4
350	51.8 [1.94]	13.80	62.1
375	125.3 [4.18]	1.00	12.5
400	80.5 [2.68]	2.20	17.6

Room temperature sheet resistance measurements were also conducted on films deposited using **1**, the findings are summarised in Table 7. Bulk resistivity values were found to be in the range of 62.1-12.5  $\mu\Omega\text{cm}$ , the lower of which approaches the value for bulk cobalt 5.6  $\mu\Omega\text{cm}$  (at 0 °C).<sup>58</sup> Films deposited at 375 °C displayed the lowest resistivity value, which may be rationalised by the high crystallinity and thickness of the film (*vide infra*). Resistivity values of thin films can be increased by a number of effects, including increasing surface roughness, a higher degree of scattering at grain boundaries and

with decreasing film thickness, electron scattering at a films surface increases.<sup>58</sup> In addition, it is likely that *ex-situ* oxidation of the films will lead to an increase in resistivity.<sup>15</sup>

## **Conclusions**

This paper reports the synthesis and thermal analysis of eleven CpCo(di-olefin) complexes and reports the first study of their use as metal deposition precursors in atmospheric pressure CVD. Because of its high thermal stability and physical properties compound **1** was identified as a potential candidate for deposition studies. Thin films were deposited onto Si substrates in the temperature range of 325-400 °C in the presence of H<sub>2</sub>. Films deposited at all temperatures were found to have very low carbon contamination by XPS analysis, with varying degrees of oxygen incorporation. The lowest measured resistivity was 12.7-17.6 μΩcm for films deposited at 375-400 °C respectively, which is in broad agreement with the purity and continuity of the films.

As indicated by XRD analysis the thin films deposited appear to be highly oriented, adopting the *fcc* crystal structure; crystallinity was found to increase proportionally with increasing deposition temperature at 375 °C after which crystallinity appears to diminish. More significantly, complex **1** represents a non-air sensitive precursor capable of depositing cobalt metal onto silicon substrates at a low enough temperature to preclude the concomitant formation of cobalt silicide.

These precursors offer significant advantages over a number of previously reported MO-CVD precursors for the production of cobalt thin films (ibid), which include the ease with which these materials can be scaled-up and modified, physical properties such as stability (thermal and chemical), the precursors general liquid nature at room temperature and relatively high vapor pressures, and finally ability to produce high purity thin films under the conditions we have described.

Further studies into the utility of several of these complexes in the CVD of Cobalt thin films at lower temperatures are presently underway.

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**Supporting Information Available:** This publication is supported by multiple datasets. Data relating to the TGA, Isothermal TGA, Volatility and XPS spectra of the films deposited at 325 °C, 350 °C, 375 °C, and 400 °C, created during this research are openly available from the University of Bath data archive at <http://dx.doi.org/10.13039/501100000266> free of charge. X-ray crystallographic files in CIF format are available free of charge *via* the internet at <http://pubs.acs.org>.

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