Half-sandwich cobalt complexes in the metal-organic chemical vapor deposition process

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ABSTRACT

A series of cobalt half-sandwich complexes of type $[Co(\eta^5\text{-}C_5H_5)(L)(L')]$ (**1**: L, L' = 1,5-hexadiene; **2**: L = $P(OEt)_3$, L' = $H_2C=CHSiMe_3$; **3**: L = L' = $P(OEt)_3$) has been studied regarding their physical properties such as the vapor pressure, decomposition temperature and applicability within the metal-organic chemical vapor deposition (MOCVD) process, with a focus of the influence of the phosphite ligands. It could be shown that an increasing number of $P(OEt)_3$ ligands increases the vapor pressure and thermal stability of the respective organometallic compound. Complex **3** appeared to be a promising MOCVD precursor with a high vapor pressure and hence was deposited onto Si/SiO_2 (100 nm) substrates. The resulting reflective layer is closed, dense and homogeneous, with a slightly granulated surface morphology. X-ray photoelectron spectroscopy (XPS) studies demonstrated the formation of metallic cobalt, cobalt phosphate, cobalt oxide and cobalt carbide.

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1. Introduction

Recently, the deposition of thin cobalt layers became of great importance due to their usage in different applications, including, but not limited to, magnetic information storage [1] and sensor systems [2]. Especially, the giant magneto resistance (GMR) effect of multilayer stacks with cobalt and non-ferromagnetic films is a fascinating field of research [3–7]. Furthermore, antibacterial coatings with thin cobalt films [8] or the application as catalyst nanoparticles for the growth of carbon nanotubes [9] are of interest. Such thin films are generated using different techniques including sputtering [10], electron beam evaporation [11,12], ALD (*Atomic Layer Deposition*) [13–19] and (MO)CVD (metal-organic chemical vapor deposition) [20–23]. Within the latter deposition technique, it could be shown that this process is capable of forming uniform cobalt films in a highly controlled manner [20–41]. In particular, MOCVD is favorable as it provides lower deposition temperatures compared to inorganic CVD [42,43]. Generally, $[Co_2(CO)_8]$ [20,21,23–26], $[Co(\eta^5\text{-}C_5H_5)]$ [23], $[Co(acac)_2]$ [27,28] and $[Co(^tBuNC(Me)NEt)_2]$ [29] are used for layer generation but those systems suffer from being, for example, toxic and are not easy to process as they are solid materials. However, liquid precursor systems such as $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ [21,23] and $[Co(CO)_3(NO)]$ [30–33] require high substrate temperatures (360-480 °C) [32,34,35] or the addition of reactive gases [30–33,36] or plasma [37,38] to ensure the formation of uniform cobalt layers.

For a series of dicobaltatetrahedranes of type $[Co_2(CO)_6(\eta^2\text{-}RC{\equiv}CR')]$ (R = H, R' = $(CH_3)_3Si$, $^nC_4H_9$, $^nC_5H_{11}$, $^nC_6H_{13}$, $^nC_7H_{15}$; R = $^nC_3H_7$, R' = $(CH_3)_3Si$, CH_3; R = R' = C_2H_5, $(CH_3)_3Si$) [39], we showed recently that a systematic modification of the functional groups R and R', respectively, enables a variation of the physical and chemical properties of the precursors in a controlled manner.

The reported synthetic pathways for $(\eta^5\text{-}C_5H_5)Co(I)$ complexes with olefins and phosphites allowed efficient access to these classes of compounds [44,45]. Herein, we present the influences of the ligands L and L' of a $[Co(\eta^5\text{-}C_5H_5)(L)(L')]$ complex with L, L' = phosphite or alkene (Chart 1) on its thermal behavior, vapor pressure and applicability within the MOCVD process. The influence of those modifications on
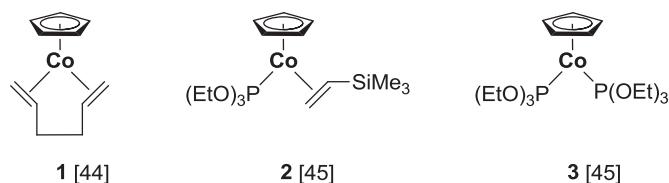

Chart 1. Cobalt precursors **1**–**3**.

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the physical properties such as the vapor pressure, the decomposition temperature and process as well as the deposition parameters during the MOCVD is investigated.

2. Experimental details

2.1. Instrumentation

Thermogravimetric measurements (TG) were performed with a METTLER TOLEDO TGA/DSC1 1100 system equipped with a UMX1 balance. Thermogravimetric coupled mass spectrometry (TG-MS) experiments were performed with a METTLER TOLEDO TGA/DSC1 1600 system with an MX1 balance coupled with a Pfeifer Vacuum MS Thermostar GSD 301T2 mass spectrometer. CVD studies were carried out using a home-built vertical cold-wall CVD reactor with a heater dimension of 20×20 mm (BACH Resistor Ceramics GmbH) [39]. Heating can be adjusted up to 773 K and is controlled by a Gefran 600 module connected with a Pt100 thermo sensor. The carrier gas (N_2) was controlled by a MKS type 247 mass flow controller connected to the reactor by heated copper lines. The CVD system was attached to a turbo molecular pump (EXC 120, EDWARDS VACUUM; base pressure: 10^{-2} Pa). Pressure control of the reactor system was performed by an EDWARDS Active Gauge Controller PKR 251. The surface morphology was investigated by field-emission scanning electron microscopy (SEM) using a ZEISS Supra60 SEM (operating voltage: 3 kV). For some of the samples, cross-sectional SEM investigations were carried out to determine the film thickness. Energy-dispersive X-ray analysis using a BRUKER Quantax 400 system attached to the SEM was applied for determining the chemical composition of the films (operating voltage: 3 keV and 10 keV). X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PREVAC XPS system with a VG Scienta EW 3000 analyzer and MX650 X-ray source, producing monochromatic Al K_α radiation.

3. Results und discussion

3.1. Thermal behavior

The volatility of cobalt(I) complexes $[Co(\eta^5\text{-}C_5H_5)(L)(L')]$ (**1**: L, L' = 1,5-hexadiene; **2**: L = P(OEt)$_3$, L' = H$_2$C=CHSiMe$_3$; **3**: L = L' = P(OEt)$_3$) was determined by vapor pressure measurements as described in reference [46]. The respective vapor pressure traces of **1**–**3** are depicted in Fig. 1; for comparison, the established precursors cobaltocene and dicobaltoctacarbonyl were measured too [39,40,47,48]. The thermal behavior of **1**–**3** was additionally studied by
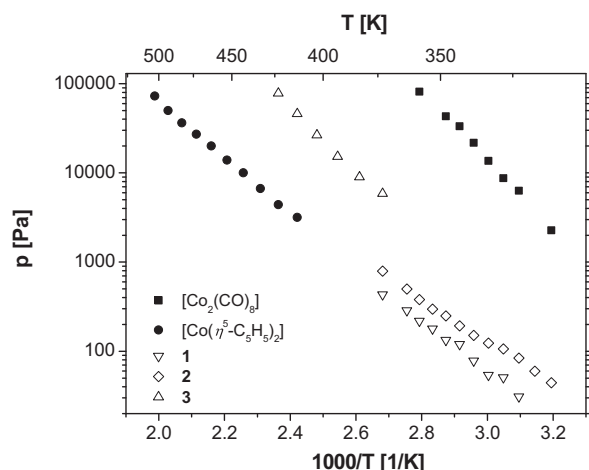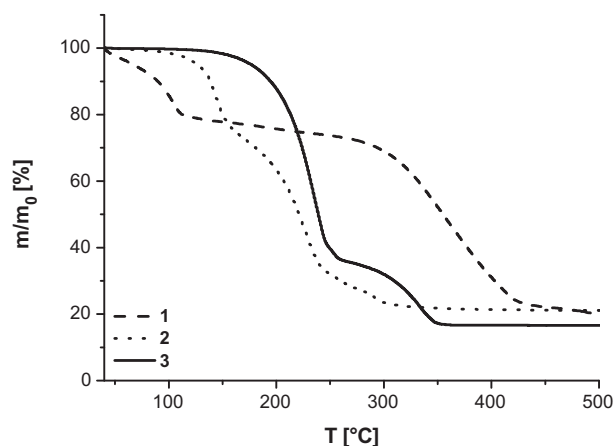
Fig. 2. TG traces of **1**–**3**; gas flow N_2 60 mL · min^{-1}, heating rate 10 K·min^{-1}.

thermogravimetric measurements (TG), and the results thereof are depicted in Fig. 2. Due to their low decomposition temperature, the vapor pressures of **1** and **2** have been measured between 40 and 100 °C, while the vapor pressure of **3** was obtained in the temperature range of 100–160 °C.

It could be shown that an increasing number of P(OEt)$_3$ ligands in **1**–**3** increases the volatility up to a vapor pressure in the range between the commonly used cobaltocene and dicobaltoctacarbonyl for **3**, while much lower vapor pressures are observed for **1** and **2**. In addition the volatility of **3** reaches values similar to $[Co_2(CO)_6(\eta^2\text{-}EtC{\equiv}CEt)]$ [39] and hence may be suitable for a MOCVD process with reasonable layer growth rates.

Thermogravimetric measurements of **1**–**3** revealed a two- or three-step decomposition (Fig. 2). The temperature range of this decomposition becomes more narrow with an increasing number of phosphite ligands present.

Thermogravimetric coupled mass spectrometry (TG-MS) experiments of **3** showed the presence of a multitude of m/z for the first weight loss step, which are summarized in Table 1 together with possible corresponding fragments. In addition, typical m/z for alkyl groups such as 29, 27, 26, 15, 14 and 12 were found. The presence of fragments containing cobalt (m/z 155, 139, 127, 111, 93, 91) highlights the high volatility of **3**. Furthermore, due to the evaporation and decomposition of **3**, fragments of the phosphite ligands (m/z 121, 93, 91, 82, 45, 31) and the cyclopentadienyl building block (m/z 66, 54) could be detected. For the second weight loss step only m/z 66, 45, 31 and typical alkyl fragments were observed. The specific decomposition mechanism is not determinable by this method due to close similarities in the fragment pattern of both steps. Nevertheless, the results allow for the

Fig. 1. Vapor pressure traces of **1**–**3** in comparison to $[Co_2(CO)_8]$ and $[Co(\eta^5\text{-}C_5H_5)_2]$.

Table 1
Detected m/z and possible corresponding fragments of TG-MS experiments of **3**.

m/z	Fragments
31	P^+
45	$C_2H_5O^+$
54	$C_4H_6^+$
66	$C_5H_6^+$
82	$PO_3H_3^+$
91	$P(OCH_2)_2^+$, $CoPH^+$
93	$CoPH_3^+$, $P(OCH_3)_2^+$
111	$PO_4CH_4^+$, $CoC_4H_4^+$
121	$P(OC_2H_5)_2^+$
127	$C_5H_5CoH_2^+$
139	$CoPH(OH)(OCH_3)^+$
155	$CoP(OH)_2(OCH_3)^+$, $C_5H_5CoP^+$