Precursor Synthesis and Thermal Studies for Cobalt Deposition

Colin Georgi, André Tuchscherer and Heinrich Lang *

Faculty of Natural Sciences, Institute of Chemistry, Department of Inorganic Chemistry, Chemnitz University of Technology, Straße der Nationen 62, 09111 Chemnitz, Germany.
E-mail: heinrich.lang@chemie.tu-chemnitz.de

Introduction

Cobalt layers are of considerable interest, due to their magnetic properties, especially, when the material size becomes comparable to the spin diffusion length. [1] In addition, thin cobalt layers are suitable as catalysts for growing single-walled carbon nanotubes. [2] Herein, we describe the straightforward synthesis of novel cobalt precursors of type $Co_2(CO)_6(\eta^2\text{-RC}\equiv\text{CR}')$ (R = $SiMe_3$; R' = H, Me_3Si, C_3H_7) and their use as CVD and ALD precursors for thin cobalt film formation. The thermal behavior of these materials is discussed in detail. Furthermore, vapor pressure measurements were carried out. Cobalt layers were formed in the temperature range between 250 and 380 °C with nitrogen as carrier gas in MOCVD cold wall reactor. The produced layers were characterized by X-Ray powder diffraction, SEM, EDX and XPS measurements.

Synthesis

For the synthesis of novel precursors **1 – 3,** $Co_2(CO)_8$ and the respective alkyne were reacted at room temperature in *n*-hexane (*Fig.* 1) within 2 h. Under elimination of two equivalents CO, a tetrahedral structure consisting of two substituted carbon atoms and two $Co(CO)_3$ fragments is formed. The compounds can be produced in nearly quantitative yields and they are insensitive to oxygen and humidity.
The substituents R and R' influenced the melting points and the vapor pressure of the appropriate dicobaltatetrahedranes.

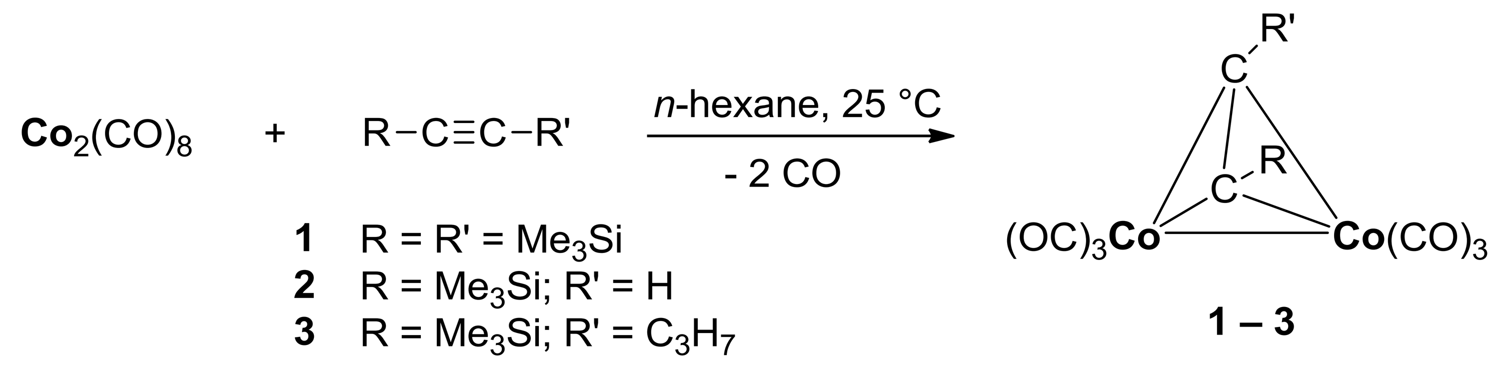

Fig. 1: Synthesis of the compounds **1 – 3**.

Physical properties of the compounds and their decomposition parameters

Thermogravimetric measurements (= TG) were carried out in a temperature range of 40 – 700 °C with a heating rate of 10 K·min^{-1} in a nitrogen carrier gas flow of 60 mL·min^{-1}.

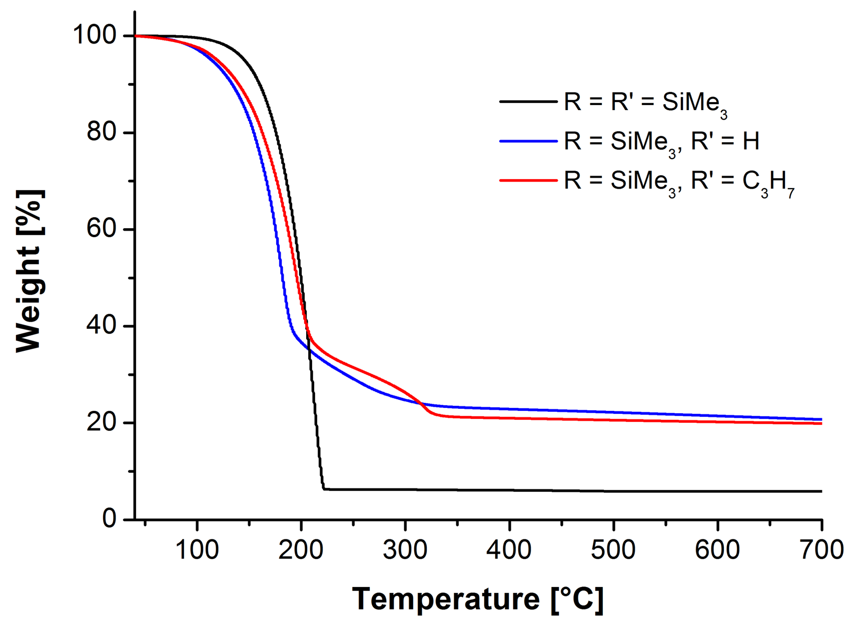

Fig. 2: TG traces of dicobaltatetrahedranes $Co_2(CO)_6(\eta^2\text{-RC}\equiv\text{CR}')$.

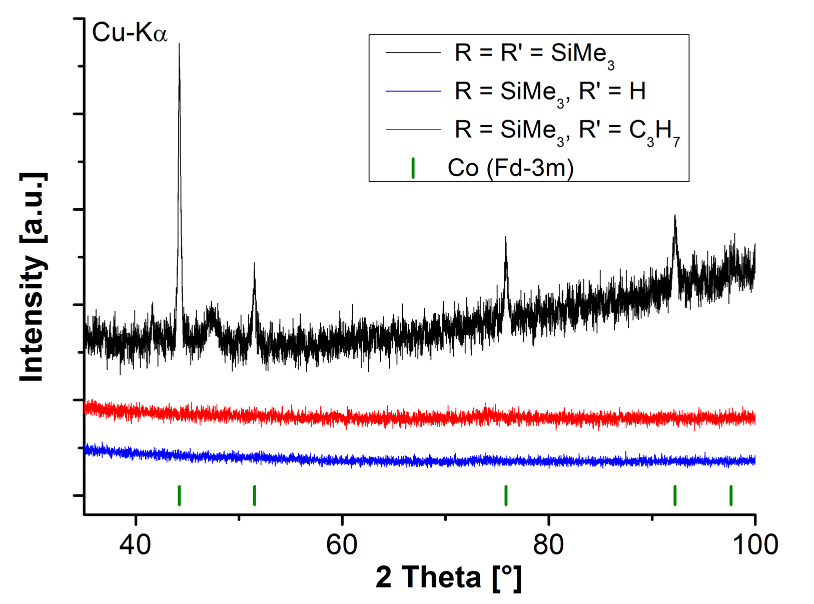

Fig. 3: XRPD pattern of the TG residues of dicobaltatetrahedranes $Co_2(CO)_6(\eta^2\text{-RC}\equiv\text{CR}')$.

Tab. 1: Cobalt amound of the dicobaltatetrahedranes $Co_2(CO)_6(\eta^2\text{-RC}\equiv\text{CR}')$

Compound	Cobalt amound
R = R' = $SiMe_3$	25.83 %
R = $SiMe_3$ R' = H	30.68 %
R = $SiMe_3$ R' = C_3H_7	27.65 %

The TG traces in *Fig.* 2 show a decomposition process in the temperature range of 150 – 350 °C. The residues were characterized by X-ray powder diffraction (= XRPD) and showed only for **1** the crystalline peaks of metallic cobalt in the space group Fm-3m as depicted in *Fig.* 3.
In addition, the resulting masses are below the cobalt values of the compounds **1** – **3** shown in *Tab.* 1. This indicates a high vapor pressure of the precursors. They are able to sublimate during the heating process. To verify this assumption, vapor pressure measurements were carried out. The results are shown in *Fig.* 4 and compared with the also measured well-known MOCVD precursors cobaltocene ((η^5-$C_5H_5)_2Co$) and dicobaltoctacarbonyl ($Co_2(CO)_8$). [3,4] The vapor pressure of **1** and **2** are in the range of cobaltocene or higher. The alkyl substituent in compound **3** tends to result in higher volatility.

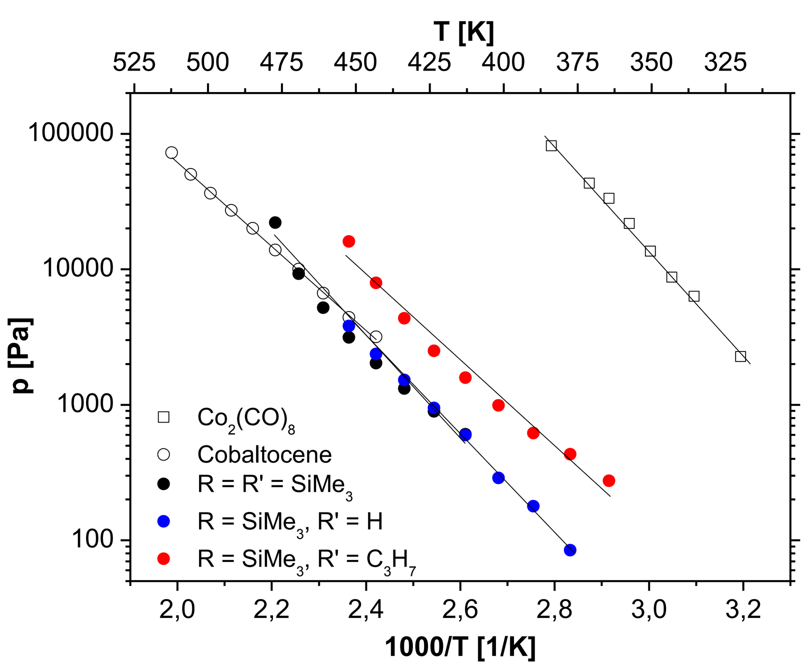

Fig. 4: Vapor pressure traces of dicobaltatetrahedranes $Co_2(CO)_6(\eta^2\text{-RC}\equiv\text{CR}')$ compared with cobaltocene and $Co_2(CO)_8$.

Tab. 2: Deposition parameters of $Co_2(CO)_6(\eta^2\text{-RC}\equiv\text{CR}')$

	1	2	3
ϑ (Precursor) [°C]	25 – 70	25	25
ϑ (Decomposition area) [°C]	250	300 – 380	350 – 380
Gasflow (N_2) [mL·min^{-1}]	50 – 75	50 – 75	0 – 75
Pressure [mbar]	0.25 – 0.6	0.25 – 1.3	0.001 – 1.3
Deposition time [min]	30	60	< 1
Layer thickness [nm]	90	70	200

Characterization of the thin metal films

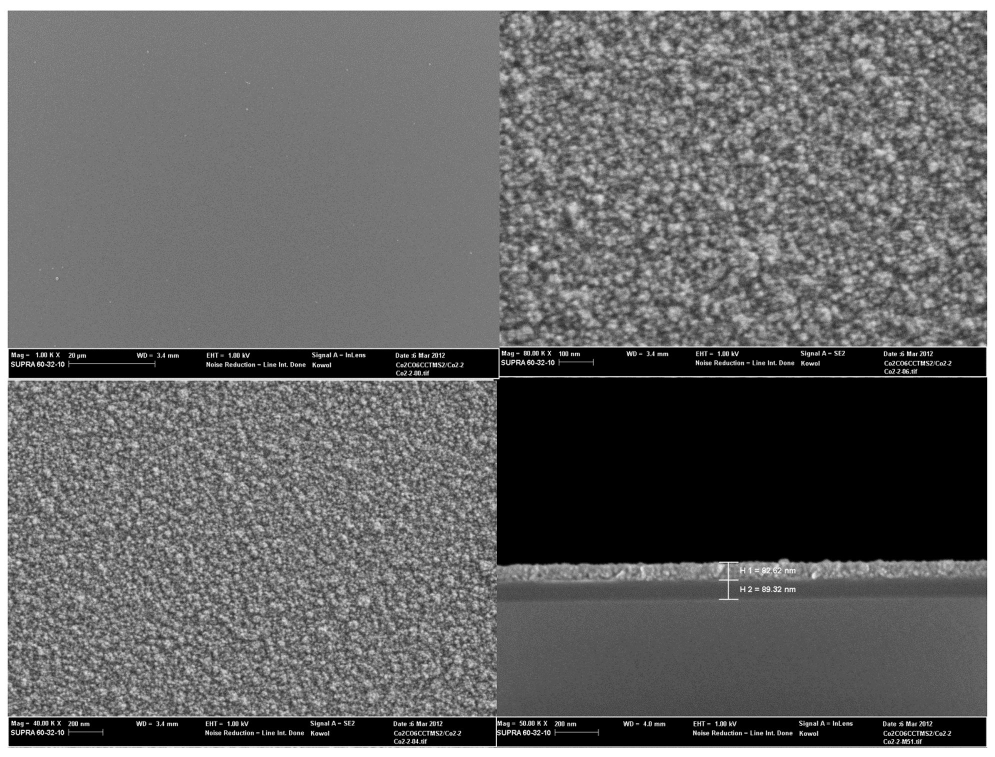

Fig. 5: SEM images of the deposited cobalt film of **1** by using the parameters given in *Tab. 2*.

The surface morphology and composition of the deposited thin films were examined by SEM and EDX measurements. From the SEM micrographs in *Fig.* 5 can be seen that the layer are smooth and dense with a thickness of 90 nm.
The different electron beam variations in the EDX measurements (10 keV and 3 keV) show characteristic peaks for cobalt, oxygen, carbon and silicon, whereas silicon is almost not present in the measurement with 3 keV (*Fig.* 6).

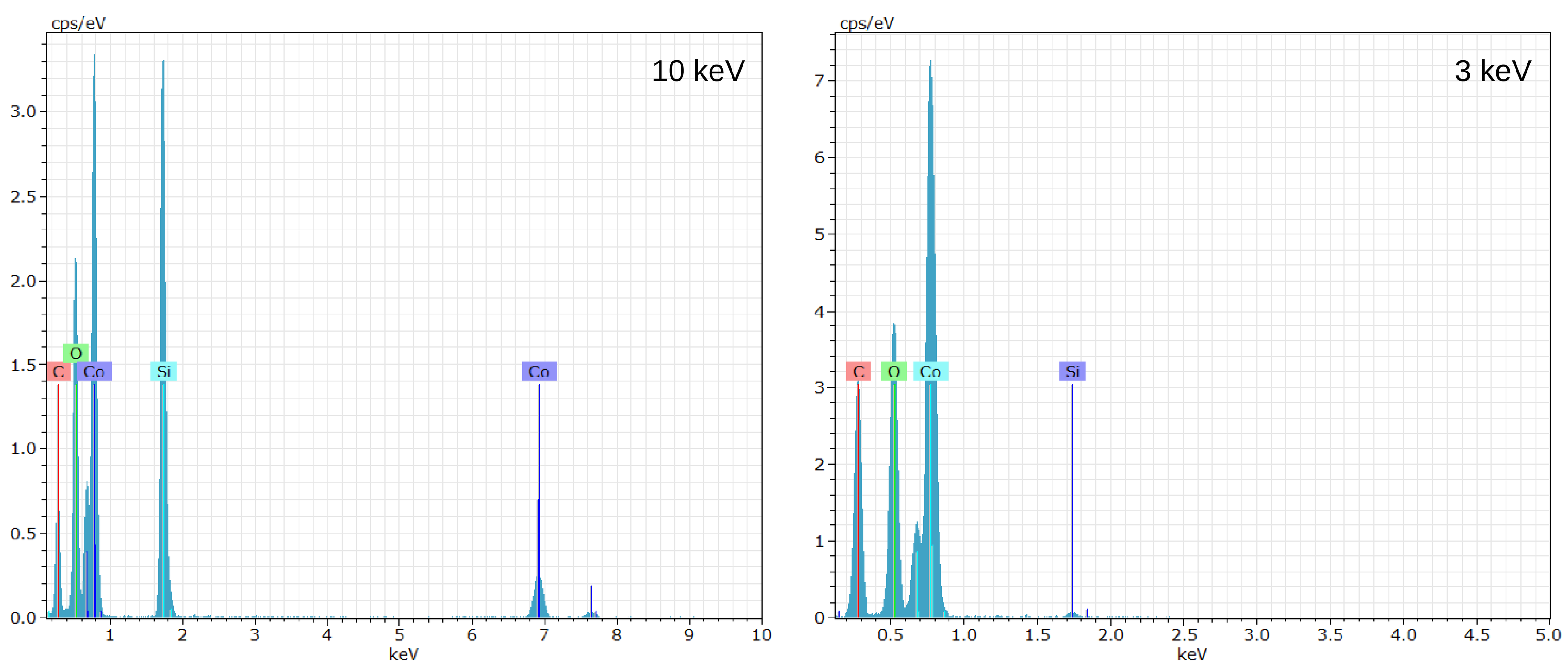

Fig. 6: EDX traces of the deposited film of **1** for different electron beam strengths.

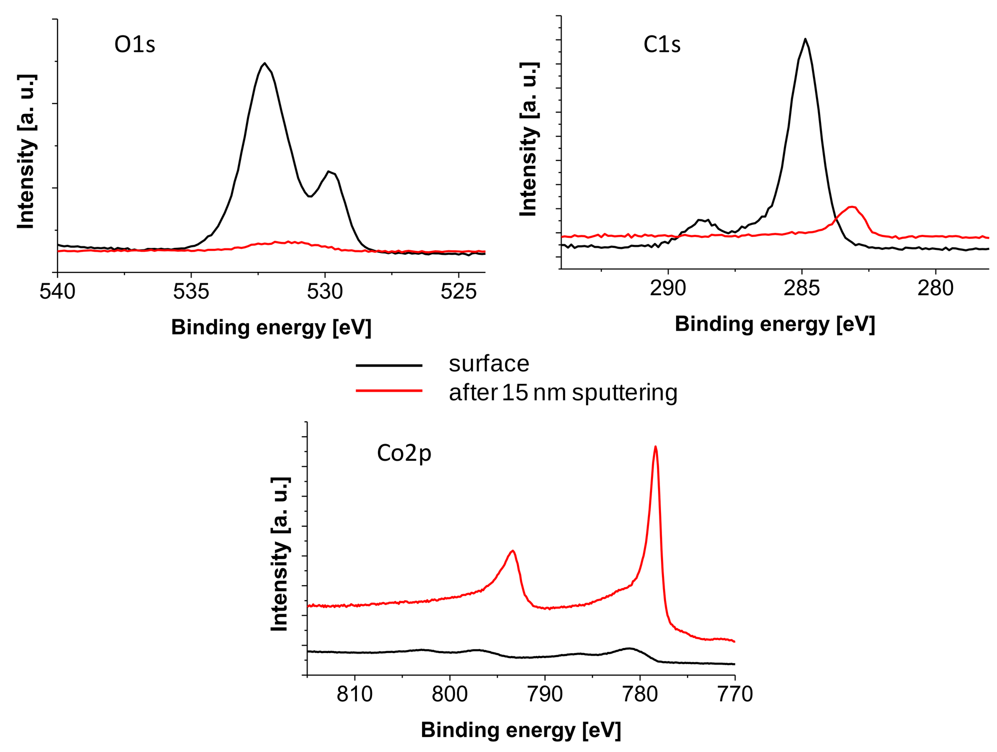

Fig. 7: XPS traces of the deposited film of **1**.

Tab. 3: Element concentration of the deposited film of **1**

	Element concentration [mol%]			
	C	O	Si	Co
Surface	34.47	26.01	5.60	33.92
Layer	2.52	0.76	0.00	96.72

From XPS measurements more information of the layer composition can be obtained (*Fig.* 7). Therefore, a comparison between the surface and the interior of the layer was carried out. The differences are significant in the values of all element concentrations. The higher amount of C, O and Si in the surface could be assigned to partially undecomposed precursor material. In the layer only cobalt and a small amount of carbon and oxygen can be found. The Si2s signal shows no silicon inside the film (*Tab.* 3).
The deposition of compounds **1**, **2** and **3** show similar results of EDX and XPS measurements. All these precursors are useful for Cobalt-CVD-Layers.

Conclusion

Novel trimethylsilyl and alkyl substituted dicobaltatetrahedranes (**1** – **3**) were synthesized and studied as potential precursors for MOCVD of cobalt. TG and vapor pressure measurements were carried out showing high volatility of the complexes and a decomposition below 350 °C. The deposition of about 100 nm thin cobalt films were carried out in a vertical home build cold wall CVD-reactor. The characterization of these layers with SEM, EDX and XPS indicate that pure, continuous and homogeneous cobalt films were formed.

References

[1] H. Lee, G. H. Gu, J. Y. Son, C. G. Park, H. Kim, *Small* **2008**, *4 (12)*, 2247-2254. [2] N. Li, X. Wang, S. Derrouiche, G. L. Haller, L. D. Pfefferle, *ACS Nano* **2010**, *4 (3)*, 1759-1767. [3] M. T. Vieyra-Eusebio, A. Rojas, *J. Chem. Eng. Data* **2011**, *56*, 5008-5018. [4] M. L. Garner, D. Chandra, *J. Phase Equilib.* **1994**, *16*, 24-29.

Acknowledgement

We gratefully acknowledge the Bundesministerium für Bildung und Forschung (NANETT, 03IS2011 - applied nano technologies for energy-efficient sensor systems) for generous financial support. In addition, we acknowledge Cornelia Kowol for SEM/EDX measurements and Dr. Steffen Oswald for XPS measurements.