

André Tuchscherer, Colin Georgi, Heinrich Lang\*

Chemnitz University of Technology, Institute of Chemistry

Department of Inorganic Chemistry, Straße der Nationen 62, 09111 Chemnitz, Germany

Prof. Dr. Heinrich Lang; Phone: +49(0)37153121210, Email: heinrich.lang@chemie.tu-chemnitz.de

## Introduction

Ruthenium and also ruthenium oxide layers are of interest for microelectronic industries, e. g. chip manufacturing, cause of their resistance to air, moisture and high temperatures. [1] Ruthenium plays a role as electrode capacitor in DRAM applications. [2] Ruthenium films can be easily etched by oxygen plasma and show good electrical properties as robust diffusion-barriers and seed layers especially for copper in integrated circuits. [3] Currently, ruthenium precursors such as carbonyls possess only poor vapor pressure in contrast to ruthenocenes, whereas, for example acetylacetonate-based ruthenium compounds evince high stability as MOCVD precursor. [1a, 4, 5] The development of new precursors for the deposition of Ru or RuO<sub>x</sub> is a great challenge. Recently, it was shown that the linkage of SiMe<sub>3</sub> groups lead to high vapour pressures of the precursors. [6] Here we describe the synthesis and thermal behaviour of novel SiMe<sub>3</sub> and <sup>t</sup>Bu based ruthenocenes and their use as CVD precursor.

## Synthesis

The development of new precursors for the deposition of Ru or RuO<sub>x</sub> is a great challenge. Recently, we were able to prepare novel Ru precursors, based on ruthenocene- and "half-open"-ruthenocene-structures. These organometallic compounds are easily available in moderate to high yields (70 – 95 %) via an one or two step synthesis procedure. The molecules are depicted in figure 1. Introduction of SiMe<sub>3</sub> (= TMS) groups on the cyclopentadienyl (= Cp) ring should achieve a melting point degradation as well as an increase of the vapor pressure. Both properties are essential requirements for a CVD precursor.

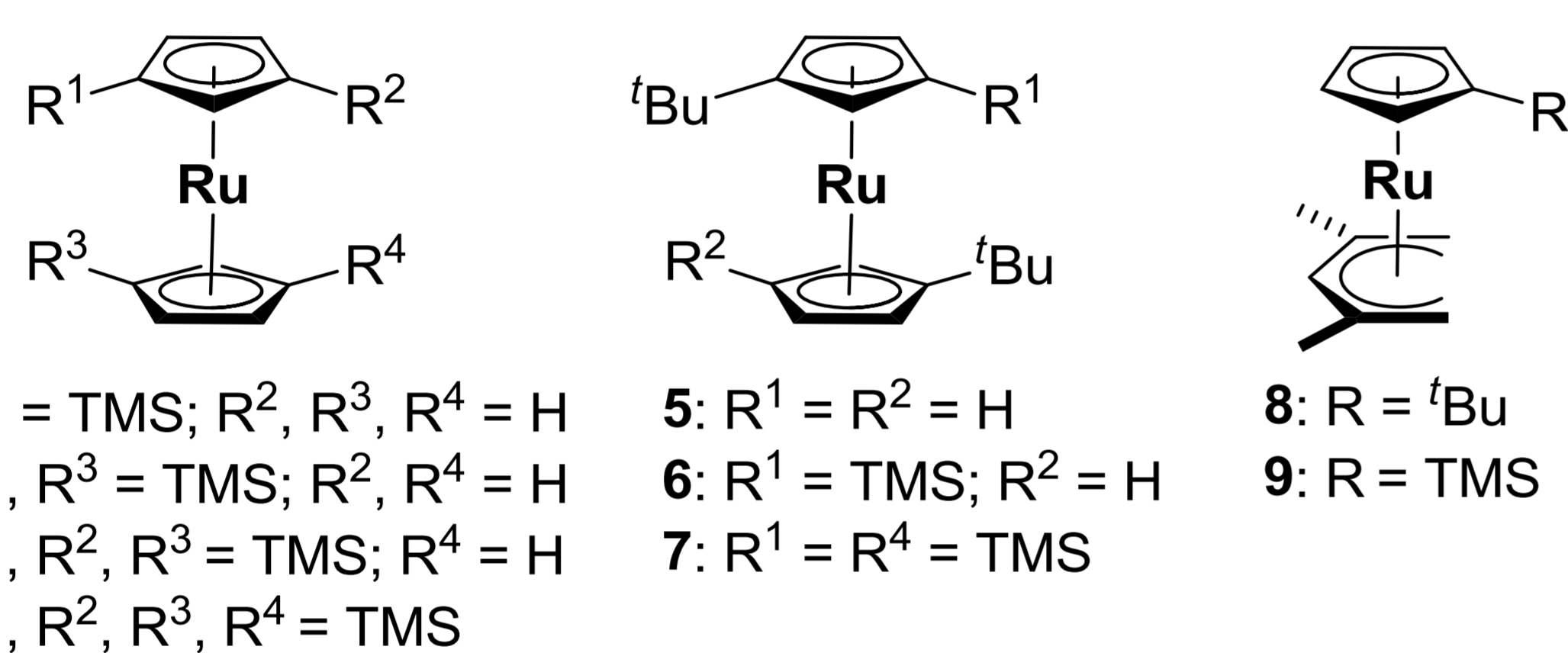


Fig.1: Overview of the different substitution pattern based on ruthenocene and half-open ruthenocene.

## Thermal Behavior

Functionalization of the ruthenocene framework with trimethylsilyl and *tert*-butyl (= <sup>t</sup>Bu) groups leads to melting point decrease for all synthesized compounds (1 - 9) in contrast to ruthenocene. This is caused by bulky SiMe<sub>3</sub> and <sup>t</sup>Bu groups which prevent a tightly packaging in the crystal structure. The most lowering is found for 8 and 9 which are liquid at ambient temperature.

TG traces (TG = ThermoGravimetry) are depicted in Fig.2. The Figure indicates that all ruthenocene systems sublime at 1 bar. This suggest that all compounds are suitable MOCVD precursors.

Tab.1: Comparison of the Onset – temperatures and Melting Points

Comp.	Onset [°C]	Melting Point [°C]
1	159	50
2	180	57
3	167	78
4	203	110
5	182	101
6	189	63
7	202	107
8	196	– a)
9	168	– a)

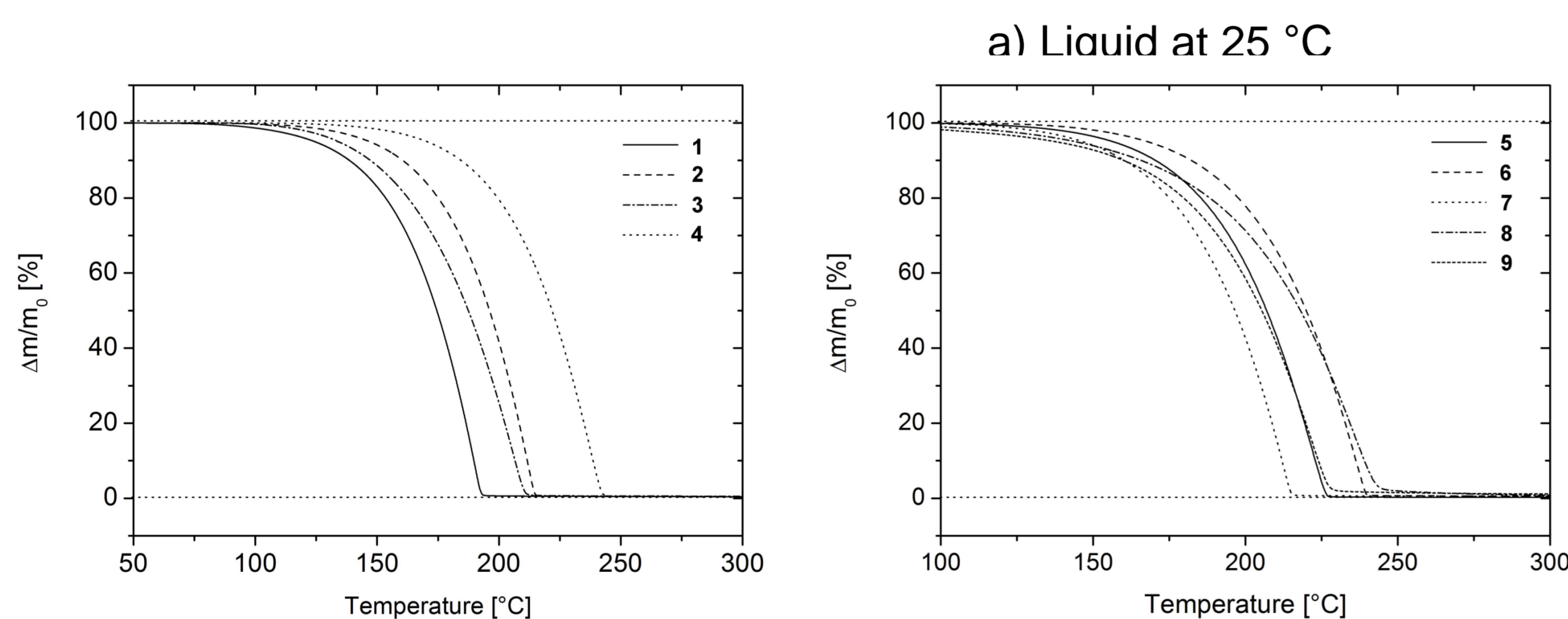


Fig.2: TGA traces of ruthenocene based precursors 1 - 4(left) and 5 - 9 (right) (N<sub>2</sub>, 1 bar, 5 K·min<sup>-1</sup>).

## Conclusion

Efficient synthetic strategies were developed to prepare new MOCVD precursors for the deposition of ruthenium on Si/SiO<sub>2</sub>. Melting point decrease was achieved by introducing SiMe<sub>3</sub> groups into the ruthenocene framework. We could lower the melting points for all compound whereas 8 and 9 are liquid at ambient temperature. A dependency of the vapor pressure on the structure was observed. Compounds 1 - 9 were successfully deposited between 360 and 415 °C using oxygen as reactive gas. Mixed layers consisting of Ru and a siliconoxide species were obtained from SiMe<sub>3</sub> containing 1, 6 and 7. However, pure ruthenium thin films were received from <sup>t</sup>Bu- substituted 5 and 9.

## References

[1] a) A. Schneider, C. Topf, U. Zenneck, *Chem. Vap. Dep.*, **2005**, 11, 99. b) K. Kawano, A. Nagai, H. Kosuge, T. Shipudami, M. Oshima, H. Funakubo, *Electrochem. Solid-State. Lett.*, **2006**, 7, C107. [2] T. Aoyama, K. Euguchi, *Jpn. J. Appl. Phys.*, **1999**, 38, L1134. [3] M. Damayanti, T. Sriharan, Z. H. Gan, S. G. Mhaisalkar, N. Jiang, L. Chan, *J. Electrochem. Soc.*, **2006**, 153, J41. [4] A. Bauer, U. Englert, S. Geyser, F. Podewils, A. Salzer, *Organomet.*, **2000**, 19, 5471. [5] a) R. H. Hill, *J. of Photopolym. Sci. Tech.*, **2006**, 19(4), 459. b) B. S. Lee, *Jpn. J. Appl. Phys.*, **1999**, 1(8), 4876. [6] M. A. Siddiqui, R. A. Siddiqui, B. Atakan, N. Roth, H. Lang, *Materials*, **2010**, 3, 1172.

## Vapor Pressure Measurements

Vapor pressure measurements were carried out to get first information of the volatility of the appropriate ruthenocene CVD precursors 1 - 9. From figure 3 it can be seen that the highest vapor pressure is found for half-open 9 containing one SiMe<sub>3</sub> substituent at the cyclopentadienyl ligand, while 8 featuring a <sup>t</sup>Bu group possesses a lower one. In contrast to 9, ruthenocene derivatives 1 - 7 show lower vapor pressures. Within the series of 1 - 7 it is obvious that 1 shows the highest vapor pressure and 4 the lowest. Palpably, the more SiMe<sub>3</sub> groups are attached to the ruthenocene framework, the lower the vapor pressures (1 - 7) are. Direct comparison of homo-disubstituted 2 (SiMe<sub>3</sub>) and 5 (<sup>t</sup>Bu) indicates that both molecules show almost the same vapor pressure. Ruthenocene 3 possesses a higher vapor pressure as 6, while 4 and 7 exhibits a contrary trend.

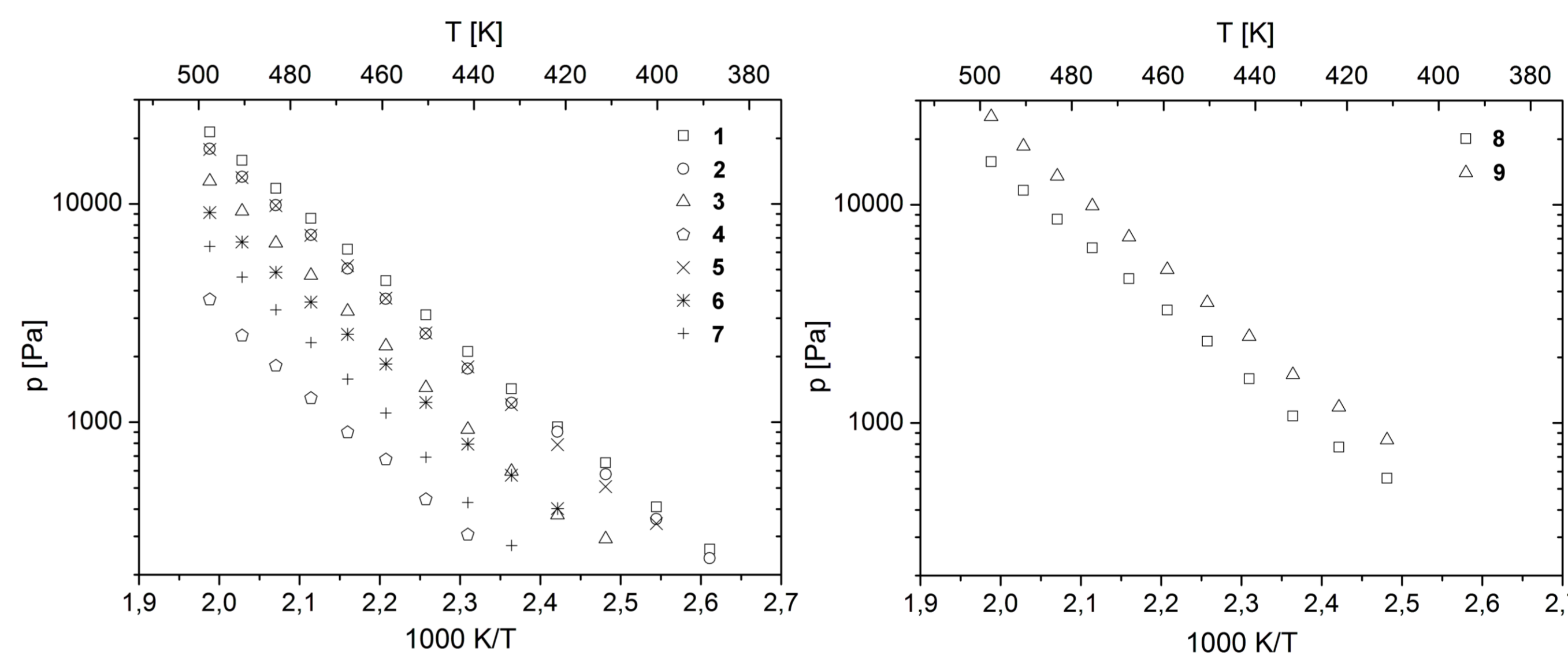


Fig.3: Vapor pressure of ruthenocenes 1 - 7(left) and half-open ruthenocenes 8 and 9 (right) (gas flow N<sub>2</sub> 60 mL min<sup>-1</sup>).

## Chemical Vapor Deposition Experiments

Chemical vapor deposition experiments using 1 - 9 as precursors were carried out with a self built vertical cold-wall reactor equipped with a continuous evaporation system. The depositions were carried out with oxygen (50 mL · min<sup>-1</sup>) as reactive and nitrogen (50 mL · min<sup>-1</sup>) as carrier gas on a silicon wafer featuring a 100 nm thick SiO<sub>2</sub> layer in a temperature range of 360 - 415 °C.

The SEM images of the deposited films are shown in figure 4. From EDX measurements the composition of the appropriate thin films was determined. For all samples the presence of the characteristic pattern of ruthenium was found. In addition, silicon, oxygen and carbon were observed. Furthermore, X-ray photoelectron spectroscopy (= XPS) was performed. To get the composition inside the films, around 15 nm of the deposits were removed by argon sputtering (3.5 keV) before starting the XPS measurements. For the layers grown by SiMe<sub>3</sub>-substituted 1, 6, 7 and 9 a high amount of silicon (14.5 – 24.5 mol%) and oxygen (37.2 – 52.7 mol%) from the Si 2p peak appearing at 103 eV was found. This peak can be unequivocally assigned to a Si-O bonding. In contrast, the layers from <sup>t</sup>Bu-substituted 5 and 8 exhibits no silicon impurities and a less amount of oxygen (5.1 – 9.0 mol%) was determined.

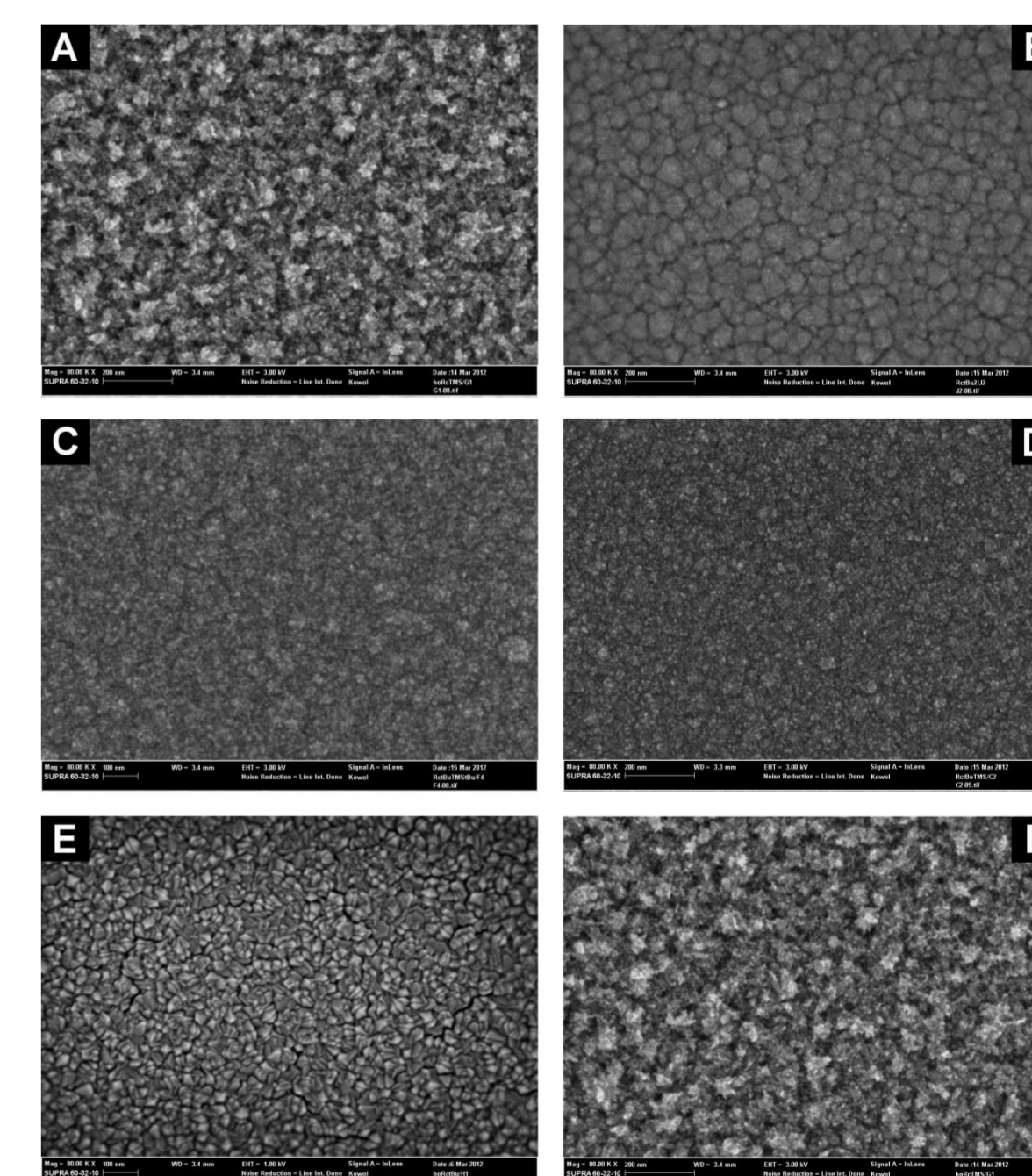


Fig.4: SEM images (magnification 40 000 x) of the deposited films: A: 1; B: 5; C: 6; D: 7; E: 8; F: 9.

## Acknowledgement

We gratefully acknowledge the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.