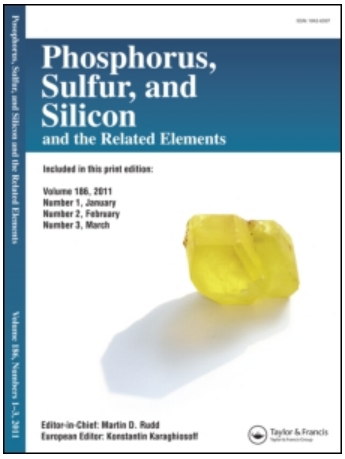

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Synthesis of Novel Transition Metal-Group 15 Cage Compounds and their Use as Molecular Precursors for Binary and Ternary Transition Metal Pnictides

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The reaction of $[\{W(CO)_5\}_2PCl]$ with $K[Co(CO)_4]$ yields the novel compounds $[W(CO)_4(\eta^4\text{-}\{Co(CO)_3P\{W(CO)_5\}\}_2)]$ **(1)** and $[\{(CO)_4WCo_3(CO)_6\}(\mu_3\text{-}P\{W(CO)_5\})]$ **(2)** along with the previously known derivatives $[Co_2(CO)_6(\mu,\eta^2\text{-}P_2\{W(CO)_5\}_2)]$ **(3)** and $[Co_3(CO)_9(\mu_3\text{-}P\{W(CO)_5\})]$ **(4)**. Complex $[W_2(CO)_8(\mu\text{-}CO)(\mu,\eta^2\text{-}P_2\{W(CO)_5\}_2)$ **(5)** was synthesised by reacting $Na_2[W_2(CO)_{10}]$ with PBr_3. Reaction of $K[Mn(CO)_5]$ with $SbCl_3$ affords $[Sb\{Mn(CO)_5\}_3]$ **(6)** in high yields. Furthermore, the thermogravimetric analysis of **1**, **4**, **5** and **6** is discussed.

Keywords: phosphorous; clusters; cobalt; tungsten; thermochemistry

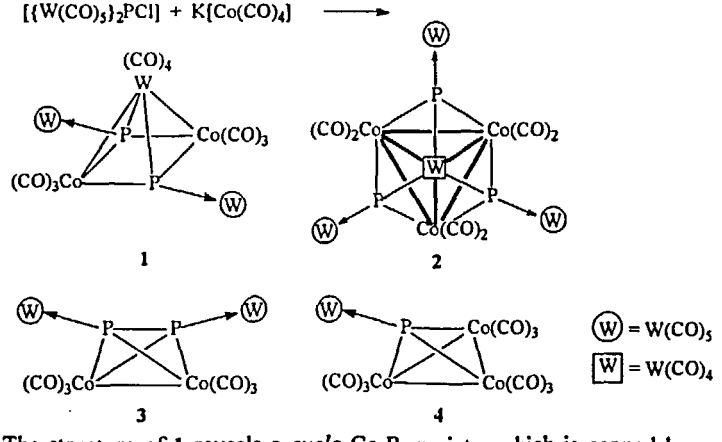
INTRODUCTION

The research area of complexes with "naked" group 15 element ligands has undergone a dynamic and exciting development [1]. The majority of publications in this field deals with the synthesis and structural features

of such E_n containing complexes (E = P, As, Sb, Bi). One of our projects in this area is directed to the use of such carbonyl containing complexes as precursors for the low temperature synthesis of novel metastable transition metal pnictides.

RESULTS AND DISCUSSION

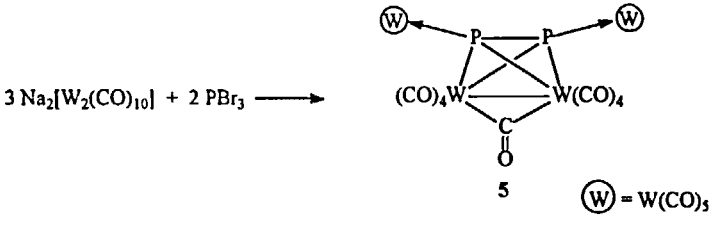
Reaction of the chlorophosphinidene complex $[\{W(CO)_5\}_2PCl]$ with $K[Co(CO)_4]$ in THF at low temperatures yields the novel products **1** and **2** as well as the previously described complexes **3** [2] and **4** [3]. The products were separated by column chromatographic work-up and were comprehensively characterised by spectroscopic methods. Additionally, X-ray structural analysis has also been carried out.



The structure of **1** reveals a *cyclo*-Co_2P_2 moiety, which is capped by a $W(CO)_4$ group. Thermogravimetric analysis (TG-MS) of **1** shows that it decomposes in two steps at 90 °C and 540 °C, respectively. In the first step CO is eliminated along with $W(CO)_6$; whereas in the second step

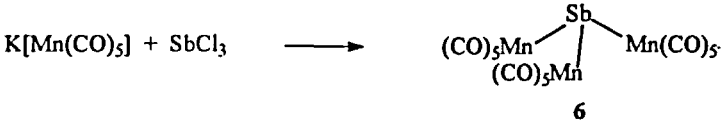
CO, P and Co is lost. Complex **2** shows a tetrahedral Co_3W cluster core. Each of the Co_2W faces is capped by a P atom, which coordinates additionally to a $W(CO)_5$ unit. Compounds **3** and **4** have already been described in the literature as the products of the analogous reaction at room temperature. The thermogravimetric analysis of **4** shows a single decomposition step at 140 °C with a weight loss of 54 %, due to the lost of CO. A possible composition of the remaining solid is Co_3WP.

The reaction of PBr_3 with $Na_2[W_2(CO)_{10}]$ in toluene at room temperature yields **5** after column chromatographic work-up. Complex **5** is the first tetrahedral W_2P_2 compound, which contains only CO ligands.



5 Ⓦ = $W(CO)_5$

The reaction of $SbCl_3$ with $K[Mn(CO)_5]$ in THF at low temperatures leads to the novel homoleptic metalastibane **6**, which has been obtained in 55% yield.



6

The thermogravimetry of **6** shows decomposition in two steps (115 °C and 180 °C), due to mainly CO elimination. The remaining solid has the composition Mn_3Sb.

The above results have shown that transition metal cluster compounds with naked group 15 elements and CO as the only ligands can be used as precursors for novel solid state compounds. Their decomposition temperatures are usually low and the composition of the remaining solids is controlled by the stoichiometry of the metals of the cluster core. Further research is necessary to get more information about the structure and the properties of these novel solid state compounds.

Acknowledgments

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