This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

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

Ulf Vogel; Manfred Scheer

To cite this Article Vogel, Ulf and Scheer, Manfred (2001) 'Synthesis of Novel Transition Metal-Group 15 Cage Compounds and their Use as Molecular Precursors for Binary and Ternary Transition Metal Pnictides', Phosphorus, Sulfur, and Silicon and the Related Elements, 169:1,223-226

To link to this Article: DOI: 10.1080/10426500108546629 URL: http://dx.doi.org/10.1080/10426500108546629

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

ULF VOGEL and MANFRED SCHEER

Institute of Inorganic Chemistry, University of Karlsruhe, D-76128 Karlsruhe, Germany

The reaction of $[\{W(CO)_5\}_2PCI\}$ with $K[Co(CO)_4]$ yields the novel compounds $[W(CO)_4(\eta^4-\langle Co(CO)_3P\{W(CO)_5\}\rangle_2)]$ (1) and $[\{(CO)_4WCO_3(CO)_6\}(\mu_3-P\{W(CO)_5\})]$ (2) along with the previously known derivatives $[Co_2(CO)_6(\mu,\eta^2-P_2\{W(CO)_5\}_2)]$ (3) and $[Co_3(CO)_9(\mu_3-P\{W(CO)_5\})]$ (4). Complex $[W_2(CO)_8(\mu-CO)(\mu,\eta^2-P_2\{W(CO)_5\}_2)]$ (5) was synthesised by reacting $Na_2[W_2(CO)_{10}]$ with PBr_3 . Reaction of $K[Mn(CO)_5]$ with $SbCI_3$ 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

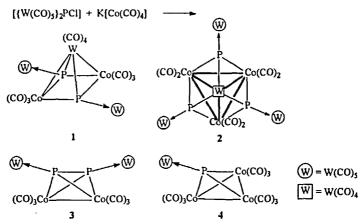
INTRODUCTION

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_a 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 prictides.

RESULTS AND DISCUSSION

Reaction of the chlorophosphinidene complex [{W(CO)₅}₂PCI] 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-Co₂P₂ 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 Co₃W cluster core. Each of the Co₂W 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 Co₃WP.

The reaction of PBr₃ with Na₂[W₂(CO)₁₀] in toluene at room temperature yields 5 after column chromatographic work-up. Complex 5 is the first tetrahedral W₂P₂ compound, which contains only CO ligands.

$$3 \text{ Na}_{2}[\text{W}_{2}(\text{CO})_{10}] + 2 \text{ PBr}_{3} \longrightarrow (\text{CO})_{4} \text{W}_{2}(\text{CO})_{4}$$

$$5 \qquad \text{W} = \text{W}(\text{CO})_{5}$$

The reaction of SbCl₃ with K[Mn(CO)₅] in THF at low temperatures leads to the novel homoleptic metalastibane 6, which has been obtained in 55% yield.

$$K[Mn(CO)_5] + SbCl_3$$

$$(CO)_5Mn$$

$$(CO)_5Mn$$

$$(CO)_5Mn$$

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 Mn₃Sb.

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

We thank Dr. W. Hönle from the Max-Planck-Institut für Festkörperforschung in Stuttgart for the TG-MS measurements and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for comprehensive financial support.

References

- Reviews: M. Scheer, E. Herrmann, Z. Chem. 29, 41 (1990); K.H. Whitmire, Adv. Organomet. Chem., 42, 1 (1998).
- [2] R. Lal De, H. Vahrenkamp, Z. Naturforsch. 40b, 1250 (1985).
- [3] H. Lang, L. Zsolnai, G. Huttner, Angew. Chem. Suppl. 1463 (1983).