Reaktionen von Vanadium(V)- und Tantal(V)-Komplexen mit kinetisch stabilisierten Phosphaalkinen. Einfache Synthese von 1,3,4-Thia- und 1,3,4-Selenadiphospholen

Reactions of Vanadium(V) and Tantalum(V)-Complexes with Kinetically Stabilized Phosphaalkynes. A Simple Synthesis of 1,3,4-Thia and 1,3,4-Selenadiphospholes

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A simple synthetic pathway to the unknown 1,3,4-thiadiphospholes **3** and 1,3,4-selenadiphospholes **4** has been developed involving reactions of the azaphosphavanada(V)-cyclobutenes **2**, generated in situ from the imidovanadium(V) complex ^{t}BuN = VCl_3 and the phosphaalkynes 1a – d, with an excess of elemental sulfur or grey selenium, respectively. The reactions of the phosphaalkynes **1a,b** with $TaOCl_3$ or $VOCl_3 \cdot$ DME furnish the 1,2-dichloro-phosphaalkenes **5a,b** and 1,2,3,4-tetrachloro-3,4-di-*tert*-butyl-1,1-diphosphethane **7a**. The metallacyclic species **2e – h** with secondary or primary alkyl groups on the ring nitrogen atom are unstable and undergo quantitative conversion to the 1*H*-1,2,4-azadiphospholes **8**, whereas in the presence of an excess of phenylacetylene the 1*H*-1,2-azaphospholes **9e – h**, are formed selectively. A catalytic reaction course has been demonstrated for the cyclotrimerization of phenylacetylene and 2-butyne initiated by small amounts of $TaSCl_3$. The syntheses of the vanadium(IV) complexes [^{t}BuN = $VCl_2 \cdot 2Py$] and [^{t}BuN = $VCl_2 \cdot$ TMEDA] are also described starting from ^{t}BuN = VCl_3 and phosphaalkene **12**.

Key words: Reactions of Phosphaalkynes, Complexes of Vanadium(V) and Tantalum(V), 1,3,4-Thiadiphospholes