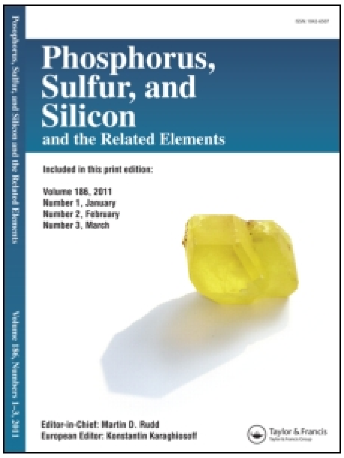

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Complexes with a Metal Phosphorus Triple Bond – a Novel Class of Highly Reactive Compounds

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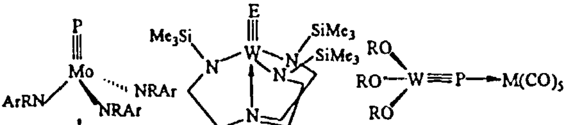
A novel approach to highly reactive phosphido complex intermediates of the type $[L_nM{\equiv}P{\rightarrow}M'(CO)_5]$ (M' = Cr, W) is achieved via the Cp* migration from a σ-bound situation at a P atom in a phosphinidene complex $[Cp^*P\{W(CO)_5\}_2]$ to the η^5-coordination at the transition metal. Consequently those compounds show a high "side-on" reactivity. Their reaction behavior with phosphaalkynes, alkynes and nitriles leads to novel metala-phosphaheterocycles. Furthermore, the use of the corresponding As analogue $[Cp^*As\{W(CO)_5\}_2]$ yields via thermolysis reaction the tetranuclear tungsten clusters, which indicate besides the formation of the triple bond intermediate $[Cp^*(CO)_2W{\equiv}As{\rightarrow}W(CO)_5]$ the occurrence of a second Cp* eliminated intermediate $[As\{W(CO)_5\}_2]$.

Keywords: P ligands; As ligands; phosphinidene; cyloadditions; cyclizations; multiple bonds

INTRODUCTION

Complexes with a metal-phosphorus triple bond are a new class of compounds [1]. In complexes of the type $[L_nM{\equiv}P]$ A the triple bond is sterically protected by bulky amido ligands as found for complexes **1** [2] and **2** [3,4], respectively. Therefore, these compounds reveal exclusively „end-on" reactivity [4,5]. Our synthetic goal has been directed towards the alkoxide substituted complexes of the type $[L_nM{\equiv}P{\rightarrow}M(CO)_5]$ **B** [6]. Thus, in complexes **3** [7] and **4** [8] the lone pair of the phosphido ligand coordinates to a Lewis-acidic carbonyl complex. The RO ligands are very flexible and thus, the metal-phosphorus triple bond remains accessible. In contrast to complexes **A** those isolable compounds show a high „side-on" reactivity.



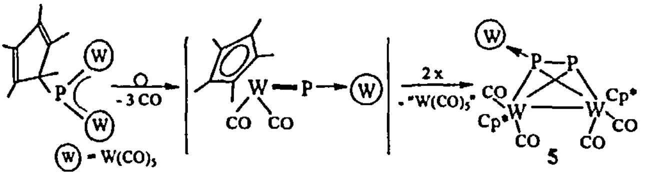
1
$R = C(CD_3)_2CH_3$
$Ar = 3,5\text{-}C_6H_3Me_2$

2a: E = P
2b: E = As

3: R = *t*Bu; M = Cr, W
4: R = Ar, M = Cr, W
$Ar = 2,6\text{-}Me_2C_6H_3$

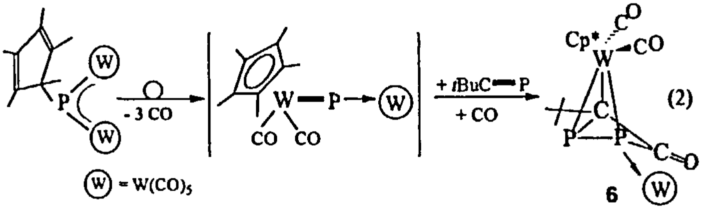
RESULTS AND DISCUSSION

Recently we developed a novel approach to complexes of type **B** as highly reactive intermediates [9]. The principle of their generation is based on a migration of a σ-bound Cp* at the phosphorus atom to give a η^5-coordination mode at the transition metal. In the absence of any reactive substrate, the intermediate stabilizes itself by dimerization to yield complex **5** (Eq. 1) [9].



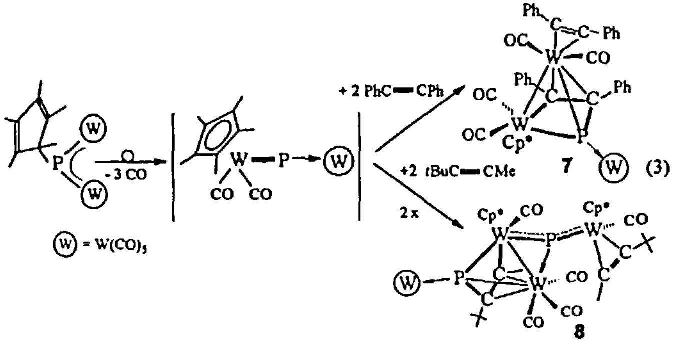
(1)

The trapping reaction chemistry of the highly reactive triple bond intermediate offers novel synthetic routes to a large variety of unprecedented metala-phosphaheterocycles. Thus, thermolysis of the phosphinidene complex $[Cp^{*}P\{W(CO)_5\}_2]$ in the presence of *t*BuC≡P yields a novel *cyclo*-diphosphabutenone ligated complex **6** (Eq. 2). By passing the phosphido complex intermediate of the type $[Cp^{*}(CO)_2W{\equiv}P{\rightarrow}W(CO)_5]$ a formal [2+2] cycloaddition occurs to give under participation of one molecule CO complex **6**.



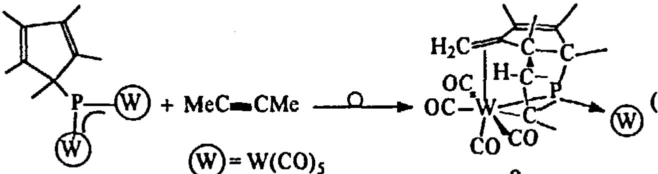
(2)

The thermolysis reactions of $[Cp^{*}P\{W(CO)_5\}_2]$ in the presence of different alkynes lead for PhC≡CPh to complex **7** and for *t*BuC≡CMe to complex **8** as the major products (Eq. 3). Both compounds indicate the formal cycloaddition reactions of the phosphido complex intermediate with the corresponding alkyne. The resulting four membered ring derivatives need a capping complex fragment for their stabilization. Thus, for the formation of **7** an external tungsten carbonyl group, whereas for **8** a second molecule of the triply bound intermediate was needed [10].



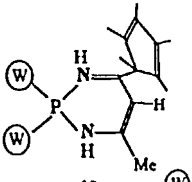
(3)

The use of MeC≡CMe leads to complex 9, which can be regarded as a trapped intermediate on the pathway of the η^1–η^5 migration of the Cp* ligand [11].



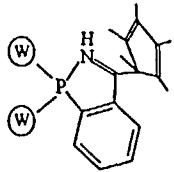
9 (4)

Additionally, reactions of [Cp*P{W(CO)$_5$}$_2$] with nitriles, such as MeCN and PhCN, were carried out at ambient temperatures. As products novel phospha-pyrimidene (**10**) and azaphosphindole (**11**) derivatives were obtained, which indicate the unusual insertion reaction of the nitriles into the P–C bond at the phosphinidene complex and additionally CH-activation reactions even at mild conditions.



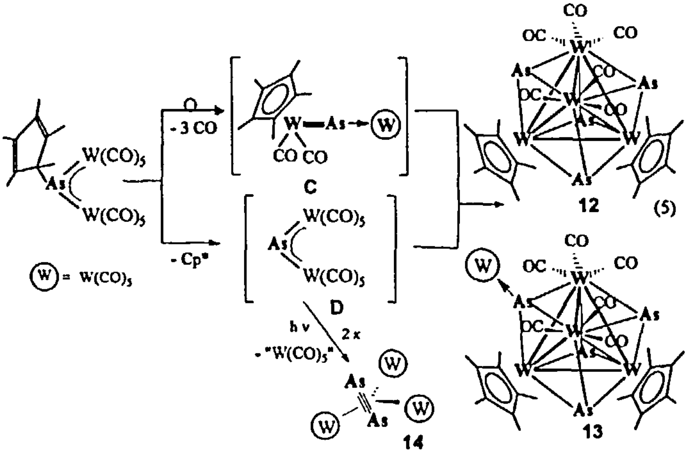
10

Ⓦ = W(CO)₅



11

The concept of the Cp* migration was furthermore extended to the heavier homologue of phosphorus, by using [Cp*As{W(CO)$_5$}$_2$] as starting material [12]. Here, via its thermolysis reaction the tetranuclear tungsten clusters **12** and **13** are formed as the major products (Eq. 5). These products show the occurrence of the arsenido triple bounded intermediate **C** as well as another intermediate **D**, resulting from a Cp* elimination process. Intermediates **C** and **D** undergo tetramerization reactions to form the cluster products. Furthermore, photolysis of [Cp*As{W(CO)$_5$}$_2$] results in the As$_2$ ligand containing complex **14**, which shows that the second pathway prevails under these conditions.



(5)

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