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## COMPLEXES WITH A METAL-PHOSPHORUS TRIPLE BOND AS VERSATILE BUILDING BLOCKS IN COORDINATION AND ORGANOMETALLIC CHEMISTRY

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reactions of the Trapping phosphidocomplex intermedigenerated $[Cp^*(CO)_2W \equiv P \rightarrow W(CO)_5],$ by thermolysis  $[Cp^*P\{W(CO)_5\}_2]$  1, occur via [2+2] cycloaddition reactions with  $P_4$ , phosphaalkynes, alkynes, and  $[CpMo(CO)_2]_2$ , respectively. However, with nitriles, insertion reactions into the P-C  $\sigma$ bond of 1 are observed already at room temperature to give novel P-containing heterocycles. Furthermore, irradiation of 1 gives the tetrahedral complex  $[Cp^*(CO)_6W_2](\mu-H)(\mu,\eta^2-P_2)\{W(CO)_5\}_2]$ , which indicates that besides the formation of the triple-bond intermediate  $[Cp^*(CO)_2W = P \rightarrow W(CO)_5]$  a second  $Cp^*$  elimination intermediate of the type  $[P\{W(CO)_5\}_2]$  occurs.

Keywords: Cyloadditions; insertion reactions; multiple bonds; P ligands

Recently we have developed a direct synthetic approach to complexes of the type  $[L_nM \equiv P \rightarrow M(CO)_5]^1$  as highly reactive intermediates. The principle of their generation is based on the migration of a  $\sigma$ -bound  $Cp^*$  at the phosphorus atom of the phosphinidene complex 1 to give an  $\eta^5$ -coordination mode at the transition metal in the formed intermediate **A**. In the absence of any reactive substrate, the intermediate stabilizes itself by dimerization to yield complex 2 (Figure 1).<sup>2</sup>

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FIGURE 1

## RESULTS AND DISCUSSION

The trapping reaction chemistry of the highly reactive triple bond intermediate  $\mathbf{A}$  is mainly characterized by [2+2] cycloaddition reactions. Thus, thermolysis of the phosphinidene complex  $[\mathrm{Cp}^*\mathrm{P}\{\mathrm{W}(\mathrm{CO})_5\}_2]$   $\mathbf{1}$  in the presence of  $\mathrm{P}_4$  phosphorus yields the cyclo- $\mathrm{P}_3$ -containing complex  $[\mathrm{Cp}^*(\mathrm{CO})_2\mathrm{W}(\eta^3-\mathrm{P}_3)]$   $\mathbf{3}$ , where  $\mathrm{P}_4$  acts as a source of " $\mathrm{P}_2$ " moieties. In the reaction with  $t\text{-}\mathrm{BuC} \equiv \mathrm{P}$  a novel cyclo-diphosphabutenone ligated complex  $\mathbf{4}$  is obtained (Eq. 2 in Figure 2). Here the cycloaddition reaction occurs with participation of one molecule CO. The thermolysis reactions of  $\mathbf{1}$  in the presence of  $\mathrm{PhC} \equiv \mathrm{CPh}$  lead to complex  $\mathbf{5}$  (Eq. 3), while use of  $[\mathrm{CpMo}(\mathrm{CO})_2]_2$  as a trapping reagent leads to the tetrahedral cluster  $\mathbf{6}$  (Eq. 4) as the major reaction products. In the case of the reaction with alkynes, after [2+2] cycloaddition, the resulting four-membered ring

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FIGURE 2

FIGURE 3

derivative needs for stabilization an external tungsten carbonyl group as capping complex fragment to form 5.3

For transition-metal complexes containing metal—metal multiple bonds like  $[CpMo(CO)_2]_2$ , metal—phosphorus and metal—metal bond formation occurs upon cycloaddition to give the tetrahedral cluster **6**.

Additionally, reactions of  $[Cp^*P\{W(CO)_5\}_2]$  with nitriles, such as MeCN and PhCN, occur already at ambient temperature. As products, the novel derivatives 1,2-dihydro-1,3,2-diazaphosphinine **7** and benzo-1*H*-1,2-azaphosphole **8** were obtained (Figure 3), which indicate the unusual insertion reaction of nitriles into the P–C  $\sigma$  bond of the phosphinidene complex and additionally CH-activation reactions even under mild conditions.<sup>4</sup>

Furthermore, irradiation of the phosphinidene complex **1** in the absence of any other substrate gives the tetrahedral complex  $[Cp^*(CO)_6W_2\}(\mu-H)(\mu,\eta^2-P_2)\{W(CO)_5\}_2]$  **9**. The product shows the occurrence of the triple-bond intermediate **A** as well as another intermediate **B**, resulting from a  $Cp^*$  elimination process (Figure 4). Intermediates **A** and **B** undergo a dimerization reaction to form the tetrahedral cluster **9**.

FIGURE 4

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