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P. Bingera; B. Biedenbacha; A. T. Herrmanna; R. Milczareka; R. Schneidera

<sup>a</sup> Max-Planck-Institut für Kohlenforschung Kaiser-Wilhelm-Platz 1, Mülheim an der, Ruhr

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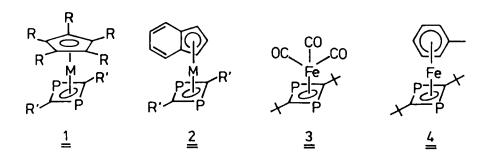
# CYCLOOLIGOMERIZATION OF $\lambda^3$ , $\sigma^1$ -phosphaalkynes in the coordination-sphere of a transition metal

P. BINGER, B. BIEDENBACH, A. T. HERRMANN, R. MILCZAREK, R. SCHNEIDER

Max-Planck-Institut für Kohlenforschung Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr

Abstract The reaction mode of phosphaalkyne cyclodimerization and codimerization with alkynes in the metal coord ination-sphere is reported.

1,3-Diphosphacyclobutadiene metal complexes of Co (1a, 2a)<sup>1-3</sup>, Rh (1b, 2b)<sup>2,4</sup>, and Fe (3, 4)<sup>5,6</sup> are now readily available by cyclodimerization of  $\lambda^3$ , $\sigma^1$ -phosphaalkynes in the coordination-sphere of these metals.



- a) M=Co; R=H,CH3; R'=i-Prop,tert.-Bu
- b) M=Rh, R=H,CH<sub>3</sub>, R'=tert.-Bu

With Co as the central metal the yields are high, ranging between 67% and  $95\%^{1-3}$ , whereas with the corresponding Rh complexes the yields are considerable lower (16 - 30%). An extensive study of the preparation of 2b showed that this is due to side reactions leading to the dinuclear Rh complex 5 and to the trinuclear Rh complex  $6^4$ .

Some insight into the mechanism of these cyclodimerizations is afforded by the isolation of a 1,4-diphospha-2-rhodacyclopentadiene derivative 7, which slowly isomerizes to the 1,3-diphosphacyclobutadiene rhodium complex 8<sup>7</sup>.

A completely new type of cyclodimer complex 9 is formed in high yields when the coordinatively unsaturated " $Cp_2Zr$ " fragment is reacted with a phosphaalkyne<sup>8</sup>. The former is easily available either by reduction of  $Cp_2ZrCl_2$  or by displacement of the ligands L from  $Cp_2ZrL_2$  (L = trimethylphosphane, 1,3-butadiene, or 1-butene).

$$Cp_{2}ZrCl_{2} + \underline{1a} \xrightarrow{Mg/HgCl_{2}} CpZr \cdots \underline{\|} \underbrace{\frac{1a}{0^{\circ}-20^{\circ}C}} Cp_{2}Zr \underbrace{Cp_{2}Zr} \underbrace{p-P} \underbrace{\frac{1a}{0^{\circ}-20^{\circ}C}} \underbrace{Cp_{2}Zr} \underbrace{p-P} \underbrace{\frac{1a}{0^{\circ}-20^{\circ}C}} \underbrace{p-P} \underbrace{p-P$$

Complex 9 is an ideal starting material for the synthesis of new heterocycles containing two phosphorus atoms. Two examples are shown in fig. 5.

$$Cp_{2}Zr \downarrow P \qquad \qquad P \qquad \qquad Cp_{2}ZrCl_{2} + 2p \qquad \qquad Cp_{2}ZrI_{2} + 2p$$

In order to achieve codimerizations between phosphaalkynes and alkynes in high yield it is neccessary to start with a preformed phosphaalkyne zirconium complex, such as complex 10. The resulting codimers are 1-phospha-3-zirconacyclo-pentadiene derivatives 11 and not 1-phospha-2,4-bicyclo[1.1.0]butanediylzirconium derivatives.

Contrary to complex 9 which can be heated to  $150^{\circ}$ C without any decomposition, the new P-C- $\sigma$ -bond of the complexes 11 is quite labile. In solution this bond is split again between 25°C and 60°C depending on the nature of the alkyne substituents. The starting complexes 10 are regained via the non detectable bis- $\pi$ -alkyne complexes in the presence of trimethylphosphanes, whereas in the absence of trimethylphosphane disproportionation occurs to give complex 9 and the corresponding 1-zirconacyclopentadiene derivatives. The recently reported 1-phospha-3-metallaindene derivatives (M = Ti, Zr)<sup>9</sup> are thermally more stable.

All new compounds are fully characterized by elementary analysis and by spectroscopic data (ms, <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P nmr). The crystal structure of many of these new complexes such as 2a<sup>2</sup>, 5<sup>4</sup>, 6<sup>4</sup>, 7<sup>7</sup>, 8<sup>7</sup>, and 9<sup>8</sup> has been also determined by an X-ray analysis.

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