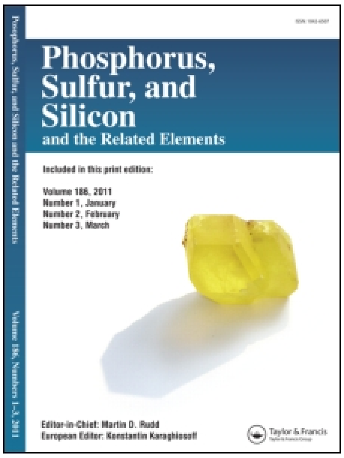

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Cyclooligomerization of $\lambda^3,^1$-Phosphaalkynes in the Coordination-Sphere of a Transition Metal

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CYCLOOLIGOMERIZATION OF λ^3,σ^1-PHOSPHAALKYNES IN THE COORDINATION-SPHERE OF A TRANSITION METAL

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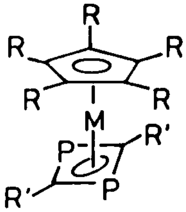
Abstract The reaction mode of phosphaalkyne cyclodimerization and codimerization with alkynes in the metal coordination-sphere is reported.

1,3-Diphosphacyclobutadiene metal complexes of Co (**1a**, **2a**)[1-3], Rh (**1b**, **2b**)[2,4], and Fe (**3**, **4**)[5,6] are now readily available by cyclodimerization of λ^3,σ^1-phosphaalkynes in the coordination-sphere of these metals.



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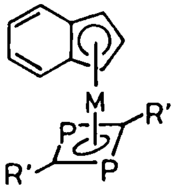

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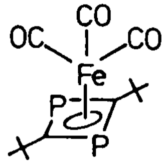

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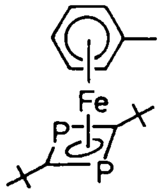

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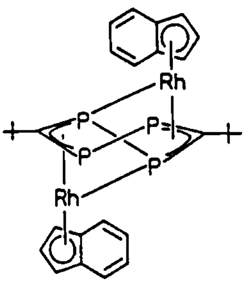
a) M = Co ; R = H,CH_3 ; R' = i-Prop ,tert.-Bu
b) M = Rh ; R = H,CH_3 ; R' = tert.-Bu

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].



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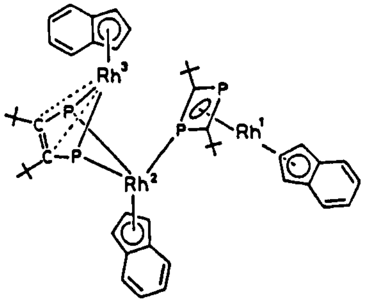

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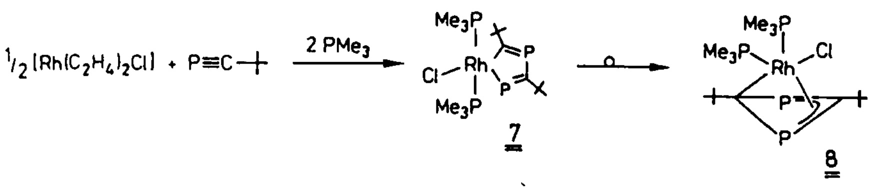
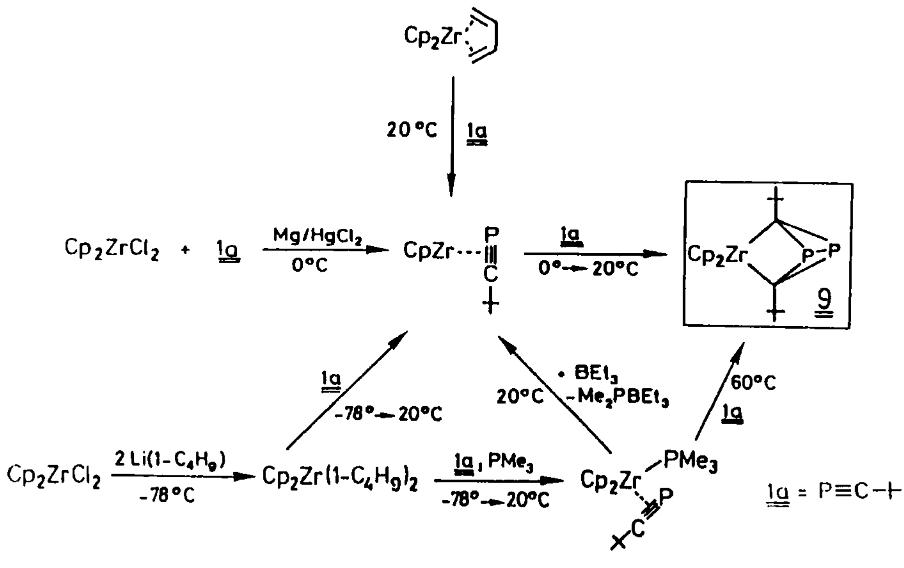
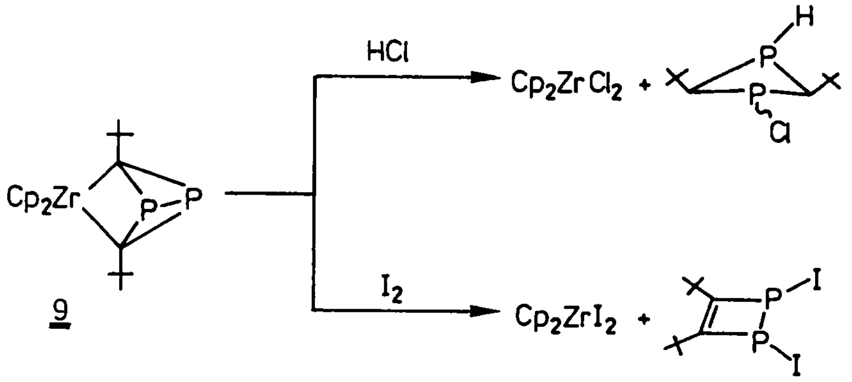
Some insight into the mechanism of these cyclodimerizations is afforded by the isolation of a 1,4-diphospha-2-rhodacyclopentadiene derivative 7, which slowly isomerizes to the 1,3-diphosphacyclobutadiene rhodium complex 8[7].



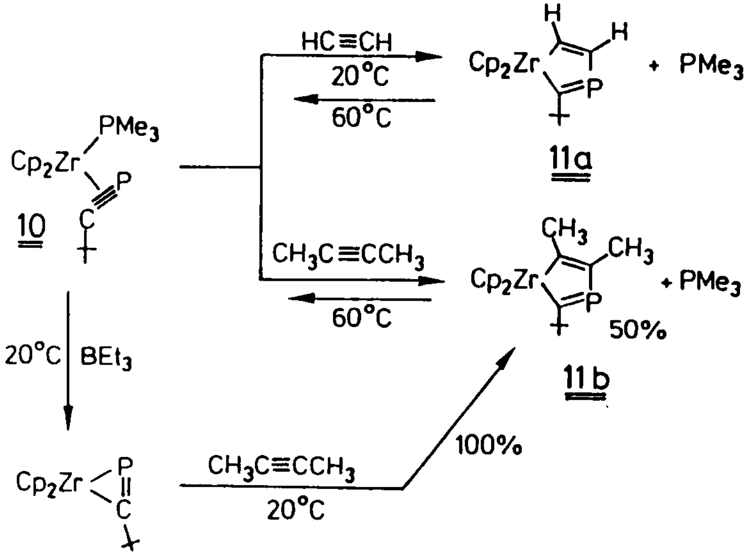
A completely new type of cyclodimer complex 9 is formed in high yields when the coordinatively unsaturated "Cp$_2$Zr" fragment is reacted with a phosphaalkyne[8]. The former is easily available either by reduction of Cp$_2$ZrCl$_2$ or by displacement of the ligands L from Cp$_2$ZrL$_2$ (L = trimethylphosphane, 1,3-butadiene, or 1-butene).



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



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–zirconacyclopentadiene derivatives **11** and not 1–phospha–2,4–bicyclo[1.1.0]butanediylzirconium derivatives.



Contrary to complex 9 which can be heated to 150°C without any decomposition, the new P–C–σ–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–π–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)[9] are thermally more stable.

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

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