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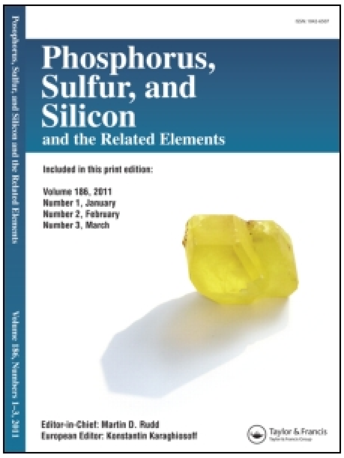

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η^8-CYCLOOCTATETRAENE METAL COMPLEXES, A NEW CLASS OF TEMPLATES FOR PHOSPHAALKYNE CYCLOOLIGOMERIZATIONS.

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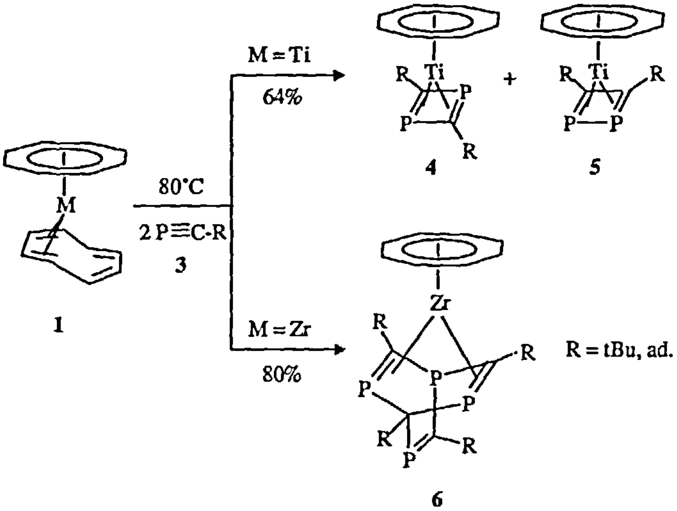
Abstract For the first time selective cyclodi-, tri-, and tetramerization of phosphaalkynes are induced by an unique class of transition metal complexes by changing the reaction conditions.

The conveniently available η^8-cyclooctatetraene early transition metal derivatives (M = Ti, Zr, Hf) such as bis(cyclooctatetraene) titanium (**1a**) and zirconium (**1b**)[1] or (η^8-cyclooctatetraene) (η^4-butadiene) zirconium **2a** and -hafnium **2b**[2] are interesting starting materials for the cyclooligomerization of phosphaalkynes (**3**). With **1a** a mixture of the η^4-1,3-diphosphete- and η^4-1,2-diphosphete titanium complexes **4** and **5** are formed after prolonged heating of **1a** and **3** to 80°C in good yield[3]. Under the same conditions **1b** leads to the formation of a new tetramer complex of **3**, the 1,3,5,7-tetraphosphabarrelene zirconium complex **6**[4] (equ. 1).

From the η^4-butadiene hafnium complex **2b** the butadiene is displaced by a phosphaalkyne **3** under much milder conditions. Moreover it depends on the reaction temperature whether di-, tri- or tetramerization of **3** occurs (see equ. 2). Thus at -78°C a new

η^8-cyclooctatetraene hafnium complex **7** is formed which contains a cyclotrimer of **3** whose bonding situation is still unknown. Complex **7** is an intermediate of the cylotetramerization of **3** which occurs at room temperature to give the hafnium complex **8**.



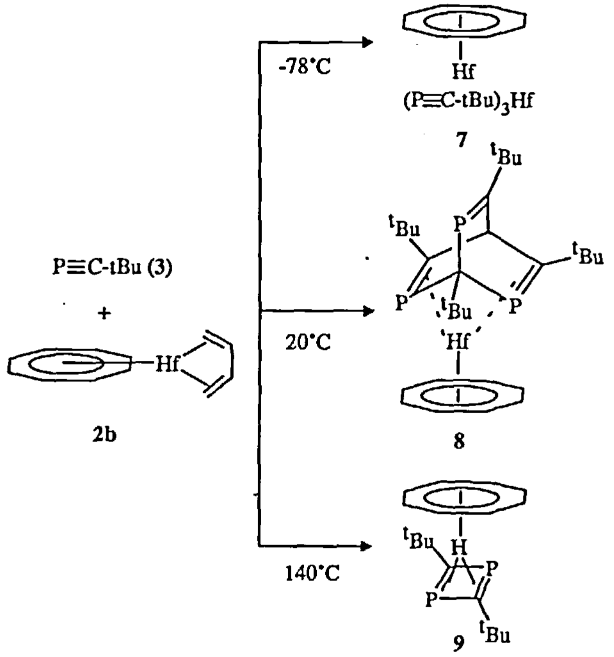
(1)

Surprisingly at higher temperature (ca. 140°C) the reaction between **2b** and **3** ends with a cyclodimerization of **3** exclusively to the 1,3-diphosphete hafnium complex **9**.

Comparable results are obtains using (η^8-1,4-bis(trimethylsilyl)cyclooctatetraene) (η^4-3-butadiene) hafnium **10** as starting material with one exceptions: the cyclotrimerization of **3** in the presence of **10**, which takes place at 0°C leads to another hafnium complex **11** in which the interaction between the cyclotrimer of **3** and the metal differs considerably from that in complex **7** (^{31}P- and ^{13}C-NMR). Presumable complex **11** contains a 7-hafna-1,3,5-diphosphanorbornadiene unit (equ. 3).

The organophosphorus part of the new hafnium complexes **7-9** and **11** is conveniently displaces by hexachloroethane in a redox reaction. In this way it was possible to synthesise for the first time 1,3,5-triphosphabenzene and 1,3,5-triphospha-Dewar-benzene derivatives **15** and **16**.

From complex **8** the recently synthesised 1,3,5,7-tetraphosphabarrelen **14** is liberated whereas complex **9** gives the undetectable 1,3-diphosphete **12** which cyclodimerise under these reaction condition to the known tetraphosphacuban **13** [5,6].



(2)

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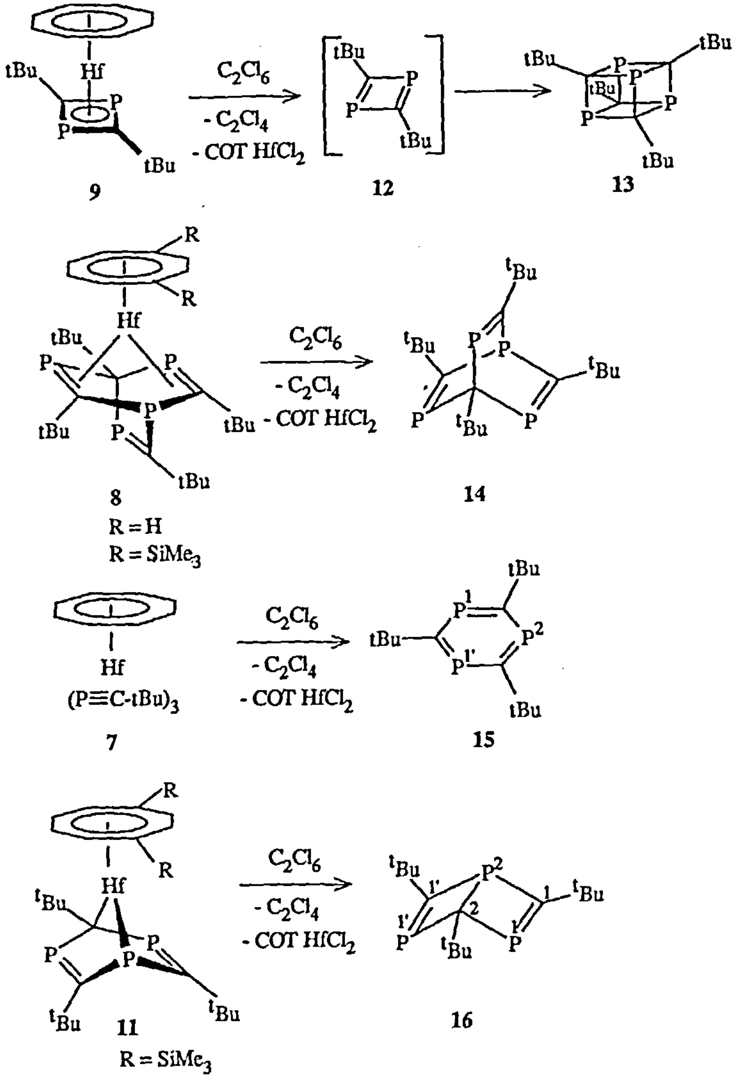
Hf
tBu
P
C$_2$Cl$_6$
- C$_2$Cl$_4$
- COT HfCl$_2$
9
12
13
R
R = H
R = SiMe$_3$
8
14
(P≡C-tBu)$_3$
7
15
11
R = SiMe$_3$
16
^{t}Bu
P^1
P^2
P$^{1'}$
1'
2
1

(3)