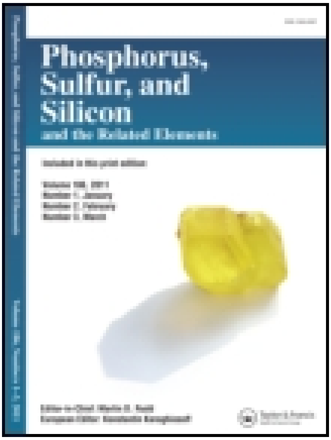

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The Metal-Initiated Cyclooligomerization of Phospha-Alkynes and its Consequences [1]

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The Metal-Initiated Cyclooligomerization of Phospha-Alkynes and its Consequences [1]

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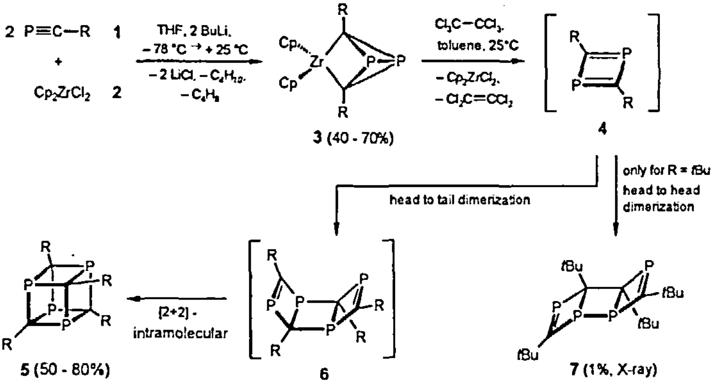
1,3-Diphosphacyclobutadienes **4** are almost certainly intermediates in the conversion by hexachloroethane of phosphaalkyne dimer complexes **3** to the tetraphosphacubanes **5**. We now describe trapping reactions of **4**, generated in the same way, with phosphaalkyne **1** (→**9**), ynamines **10** (→**13**), and electron-poor alkynes **11** (→**14**). The cyclooligomerization of **1** initiated by *t*-Bu-N=VCl_3•DME (**15**) leads to the azatetraphosphaquadricyclanes **20** while the reaction with the stronger Lewis acid *t*-Bu-N=VCl_3 (**21**) furnishes the 1,3,5-triphosphabenzenes **23** in high selectivity.

INTRODUCTION

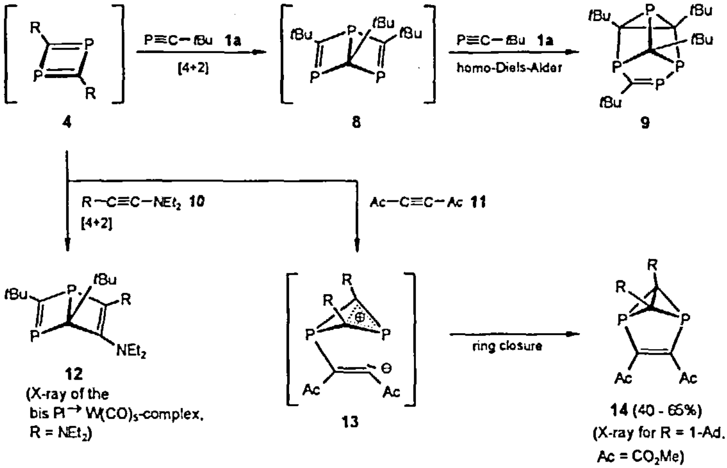
Phosphaalkynes **1** undergo cyclodimerization with Cp_2ZrCl_2 (**2**) in the presence of *n*-BuLi to furnish the tricyclic dimers **3** with incorporation of the Cp_2Zr fragment [2]. Removal of the latter fragment by treatment with hexachloroethane (formation of Cp_2ZrCl_2 and Cl_2C=CCl_2) results in the tetraphosphacubanes **5** in very good yields [3, 2b].



We assume that P/P bond cleavage to afford the 1,3-diphosphacyclobutadienes **4** occurs after removal of the Cp_2Zr fragment from **3** and that **4** then undergoes isomerization to the cage compound **5** via tetraphosphatricyclooctadiene **6** and intramolecular [2+2]cycloaddition. In the case of **4** (R = *t*-Bu), the chair-like head-to-head dimer **7** of the antiheteroaromatic species was isolated and its structure elucidated [4]. We show now by trapping experiments that **4** is an intermediate in the formation of **5**. In the second part of this note we discuss cyclooligomerizations of phosphaalkynes **1** mediated by *t*-Bu–N=VCl_3: while use of the DME complex **15** leads to the formation of azatetraphosphaquadricyclanes **20**, reactions with the free reagent **21** afford 1,3,5-triphosphabenzenes **23** [5].

RESULTS

When **4** (R = *t*-Bu) is generated from **3** (R = *t*-Bu) as described but in the presence of multiple bond systems, the intermediately formed 1,3-diphosphacyclobutadiene can be trapped unequivocally. When two equivalents of phosphaalkyne **1** (R = *t*-Bu) are used the Dewar-1,3,5-triphosphabenzene **8** is formed initially [6] and then participates in a homo-Diels-Alder reaction with the second equivalent of **1** to give the tetraphosphatetracyclooctene **9**, the structure of which was confirmed by an independent synthesis [7].

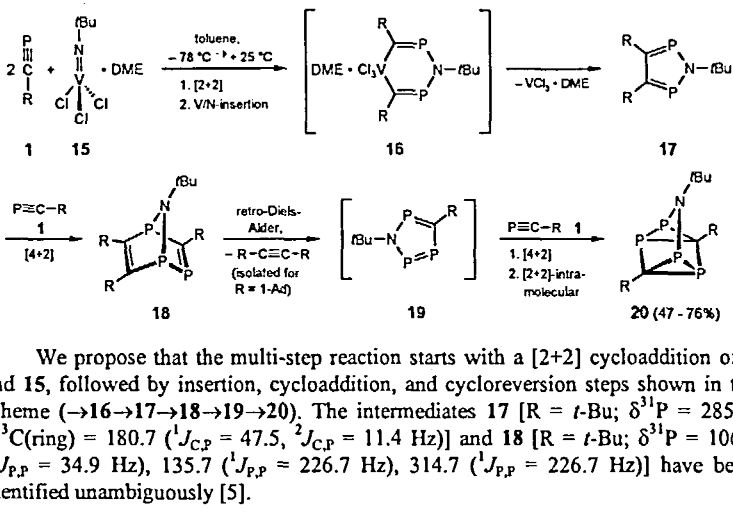


(X-ray of the bis P¹→W(CO)₅-complex, R = NEt₂)

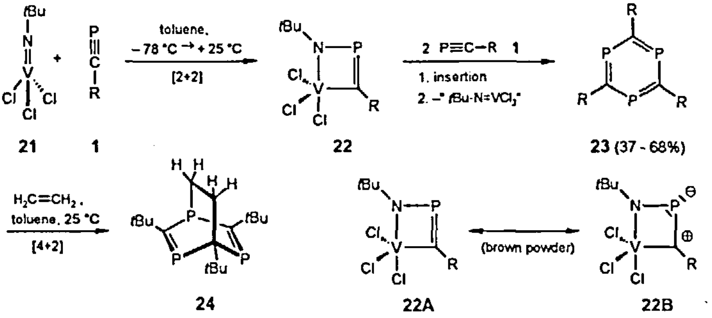
(X-ray for R = 1-Ad, Ac = CO_2Me)

Trapping reactions with ynamines stop at the stage of the Dewar-1,3-diphosphabenzenes **12**. An X-ray crystal structure determination of the bis(pentacarbonyltungsten) complex of **12** (R = NEt_2) irrevocably confirmed the proposed bicyclic structure. Finally, trapping reactions of **4** (R = *t*-Bu) with electron-poor alkynes **11** were realized; they led to the 2,5-diphosphabenzvalenes **14** which, like their valence isomeric Dewar derivatives, were previously unknown [6]. It is clear that a hetero-Diels-Alder reaction cannot be responsible for product formation in these cases. A more probable mechanism is that **4** attacks the electron-deficient triple bond of **11** as a phosphorus nucleophile with generation of betaine **13** which is then responsible for formation of the diphosphabenzvalene **14** in the subsequent cyclization step. The structure of the diphosphatricyclohexenes has been confirmed by X-ray crystallography for **14** (R = 1-Ad) [6].

Cyclooligomerization of phosphaalkynes **1** with the vanadium compound **15** furnish the azatetraphosphaquadricyclanes **20** in good selectivity [6]. Four equivalents of phosphaalkyne **1** and the imido group of **15** are incorporated in the product with loss of 2 RC units (as an acetylene which has been isolated and identified in the case of R = 1-Ad). This result has been confirmed by X-ray crystallography of **20** (R = *t*-Bu) [6].



We propose that the multi-step reaction starts with a [2+2] cycloaddition of **1** and **15**, followed by insertion, cycloaddition, and cycloreversion steps shown in the scheme (→**16**→**17**→**18**→**19**→**20**). The intermediates **17** [R = *t*-Bu; $\delta^{31}P$ = 285.7; $\delta^{13}C$(ring) = 180.7 ($^1J_{C,P}$ = 47.5, $^2J_{C,P}$ = 11.4 Hz)] and **18** [R = *t*-Bu; $\delta^{31}P$ = 106.1 ($^2J_{P,P}$ = 34.9 Hz), 135.7 ($^1J_{P,P}$ = 226.7 Hz), 314.7 ($^1J_{P,P}$ = 226.7 Hz)] have been identified unambiguously [5].



In surprising contrast, reactions of phosphaalkynes **1** with **21** (molar ratio ≅ 4:1) yield the 1,3,5-triphosphabenzenes **23** [5]. The 1:1 adducts, presumably with the four-membered ring structure **22**, undoubtedly occur as intermediates. For example, the *t*-Bu derivative can be isolated as a brown powder [correct elemental analysis, $\delta^{31}P = -73$, $\delta^{13}C(\text{ring}) = 314.2$], but does not provide any further information about P,C coupling with the two *t*-Bu groups because of the quadropole properties of vanadium. The high field position of the phosphorus signal and the extremely low field position of the ring carbon signal are only compatible with an electron distribution according to **22A↔22B**. No firm conclusions about intermediates in the further course of the cyclotrimerization are possible.

The 1,3,5-triphosphabenzenes [8], which are now accessible by a simple route, serve as excellent dienophiles in Diels-Alder reactions: stilbene, norbornene, and even ethene itself undergo smooth addition to furnish dihydrobarrelenes (e.g., **24**).

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