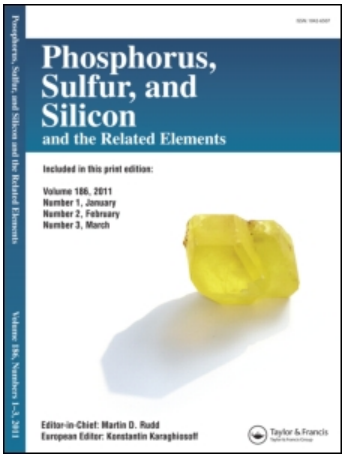

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DIRECTED SYNTHESIS OF PHOSPHORUS-CARBON CAGE COMPOUNDS — A CHALLENGE IN ORGANOPHOSPHORUS CHEMISTRY [1]

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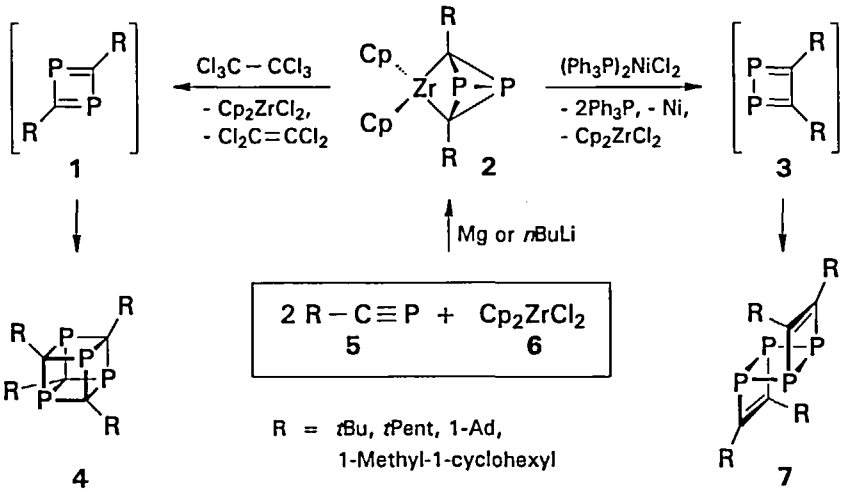
Abstract Reactions of the zirconium complexes **2** with hexachloroethane lead to the tetraphosphacubanes **4** whereas extrusion of the Cp_2Zr units by means of $(Ph_3P)_2NiCl_2$ gives rise to the tetraphosphacyclooctadienes **7**. Polycyclic phosphorus-carbon systems such as **11** or **14** and **13** are accessible from multi-step reactions of the phosphaalkyne **5** (R = *t*-Bu) with dienes **9** or tropone (**10**), respectively. The complex **16** obtained from the spirocyclotrimerization of the phosphaalkyne **5** (R = *t*-Bu) with aluminum trichloride provides the starting point for the construction of the bis(homo)prismane **19** and the hexaphosphapentaprismane **20**. Furthermore, the phosphorus-carbon-aluminum cage compounds **12**, **23**, and **24** have been prepared from the phosphaalkynes **5** and the triorganoaluminum reagents **22**.

INTRODUCTION

In contrast to their all-carbon or all-phosphorus analogs, phosphorus-carbon cage compounds have only become accessible in the past few years and the phosphaalkynes **5** have proved to be indispensable starting materials. Both purely thermal cyclooligomerization reactions of the latter to furnish tetraphosphacubanes and -cuneanes as well as the corresponding reactions in the presence of organometallic auxiliaries and the coupling reactions of di- and triphosphacyclopentadienides with platinum(II) species are unselective and provide merely modest yields [2]. In this communication, we present reaction strategies for the specific syntheses of phosphorus-carbon polycyclic systems in good to excellent yields.

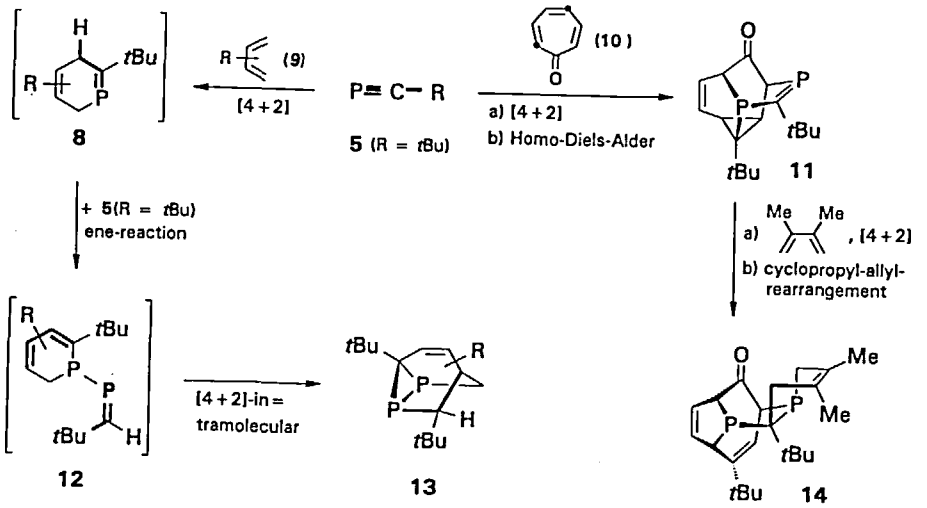
RESULTS

The specific synthesis of tetraphosphacubanes **4** starts from the zirconocene-phosphaalkyne dimer complexes **2** which, in turn, are accessible from zirconocene dichloride (**6**) and two equivalents of the phosphaalkyne **5** in the presence of magnesium or *n*-butyllithium [3].



Treatment of the complexes **2** with hexachloroethane effects removal of the zirconocene fragment to afford, after a further dimerization, the pentacyclic product **4** [3]. On the other hand, when the complexes **2** are treated with $(Ph_3P)_2NiCl_2$ instead of hexachloroethane, the tetraphosphatricyclooctadienes **7** containing a central P_4 unit are obtained. The 1,3- and 1,2-diphosphetes **1** and **3** are putative intermediates on the way to the polycyclic products [4].

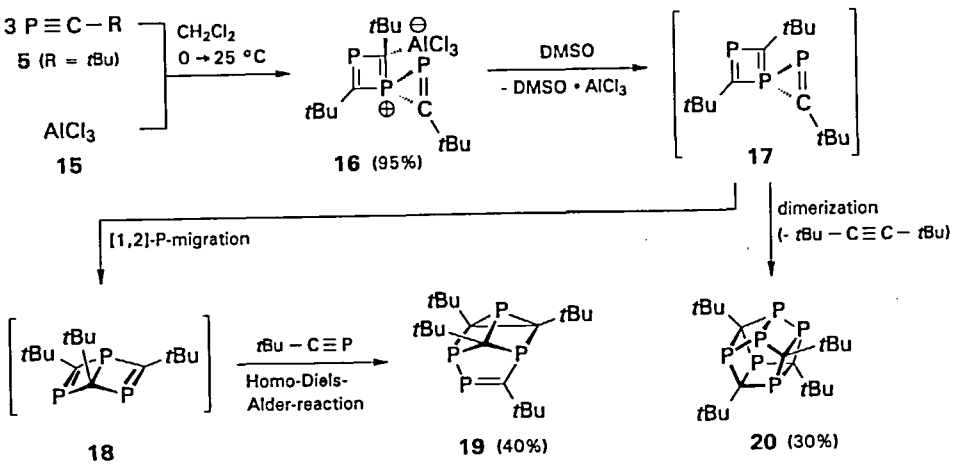
Reaction sequences initiated by Diels-Alder reactions of phosphaalkynes have opened up previously unimagined possibilities for the synthesis of phosphorus-carbon cage compounds.



Thus, reactions of the dienophile **5** (R = *t*-Bu) with variously substituted 1,3-butadienes **9** in a molar ratio of 2:1 furnish the diphosphatricyclooctenes **13** in optimum yields. The reaction mechanism involves an initial [4 + 2]-cycloaddition, an ene reaction with the second equivalent of **5** to give the cyclohexadienylphosphaalkene **12**, and spontaneous isomerization of the latter through an intramolecular Diels-Alder reaction to yield the polycyclic product [5].

With the same stoichiometry, the initial reaction of **5** (R = *t*-Bu) with tropone (**10**) affords the Diels-Alder adduct which then reacts with the second equivalent of **5** in a homo-Diels-Alder reaction to provide the diphosphatetracycloundecadienone **11** [6]. The dienophilic properties of such compounds can be exploited for the construction of further polycyclic species (e.g. **11** → **14**); in this process the cycloaddition of the 1,3-diene is followed by a sterically initiated cyclopropyl-allyl rearrangement [6].

In the presence of Lewis acids such as aluminum trichloride in a molar ratio of 1:3, the phosphaalkyne **5** (R = *t*-Bu) undergoes spirocyclotrimerization to furnish the 1-$\lambda^3\sigma^2$,3-$\lambda^4\sigma^4$-diphosphete-$AlCl_3$ adduct **16** [7].

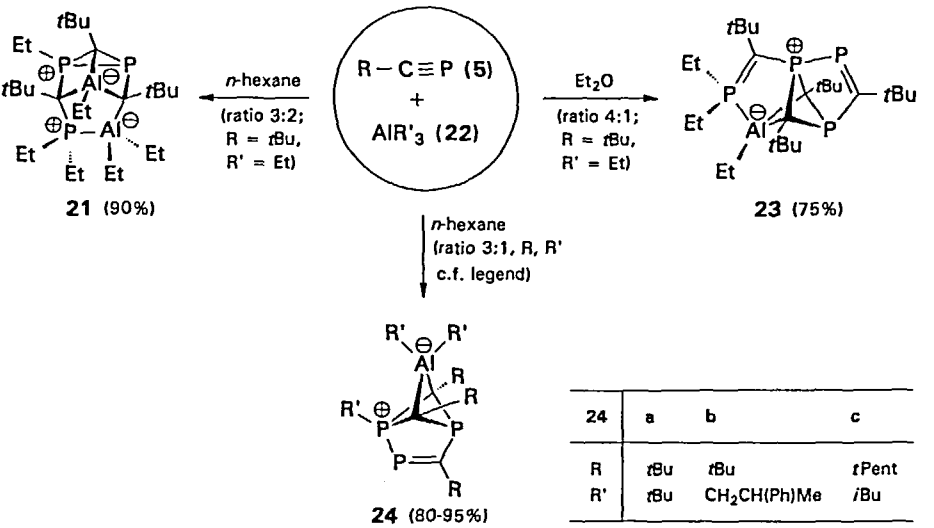


When the more energy-rich spirocyclotrimer **17** is liberated from **16** by treatment with DMSO as a Lewis base, it can only be detected by indirect methods: in dichloromethane at −45 °C rearrangement by [1,2]-P/P migration takes place to furnish the Dewar 1,3,5-triphosphabenzene **18** which, under the prevailing conditions, can only be trapped as **19** after a homo-Diels-Alder reaction with further **5** [7]. In the absence of a trapping reagent, **17** dimerizes with loss of di-*t*-butylacetylene to the hexaphosphapentaprismane **20** [8].

When phosphaalkynes are allowed to react with triorganoaluminum reagents, the latter are incorporated into the reaction products; solvent effects and the size of the substituents in the Lewis acid determine the product palette.

In the non-polar solvent *n*-hexane (molar ratio **5**:**22** = 3:2) with moderately large AlR'_3 substituents (R′ = Me, Et), the bis(homo)prismanes **21** with two-fold phosphonium-aluminate character are formed. In the more polar solvent diethyl ether (molar ratio 4:1), the tetracyclic products **23** are produced, again in high selectivity (yields in all cases ≥

75%!) [9]. Voluminous substituents at aluminum (molar ratio 3:1) result in the formation of the triphosphahomobenzvalenes **24** [10].



24	a	b	c
R	*t*Bu	*t*Bu	*t*Pent
R'	*t*Bu	$CH_2CH(Ph)Me$	*i*Bu

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REFERENCES

1. Organophosphorus compounds 108; for part 107, see: R. Armbrust, M. Sanchez, R. Reau, U. Bergsträsser, M. Regitz, G. Bertrand, *J. Am. Chem. Soc.*, **117**, in press (1995).
2. Short review: R. Streubel, *Angew. Chem.*, **107**, 478 (1995); *Angew. Chem., Int. Ed. Engl.*, **34**, 436 (1995).
3. B. Geissler, T. Wettling, S. Barth, P. Binger, M. Regitz, *Synthesis*, 1337 (1994); and references cited therein.
4. B. Geissler, S. Barth, U. Bergsträsser, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. v. R. Schleyer, M. Regitz, *Angew. Chem.*, **107**, 485 (1995); *Angew. Chem., Int. Ed. Engl.*, **34**, 484 (1995).
5. H. Heydt, U. Bergsträsser, R. Fässler, E. Fuchs, N. Kamel, T. Mackewitz, G. Michels, W. Rösch, M. Regitz, P. Mazerolles, C. Laurent, A. Faucher, *Bull. Soc. Chim. Fr.*, in press (1995).
6. M. Julino, U. Bergsträsser, M. Regitz, *J. Org. Chem.*, **60**, in press (1995).
7. B. Breit, U. Bergsträsser, G. Maas, M. Regitz, *Angew. Chem.*, **104**, 1043 (1992); *Angew. Chem., Int. Ed. Engl.*, **31**, 1055 (1992).
8. M. Regitz, B. Breit, University of Kaiserslautern, unpublished results (1992).
9. B. Breit, A. Hoffmann, U. Bergsträsser, L. Ricard, F. Mathey, M. Regitz, *Angew. Chem.*, **106**, 1541 (1994); *Angew. Chem., Int. Ed. Engl.*, **33**, 1491 (1994).
10. M. Regitz, A. Hoffmann, University of Kaiserslautern, unpublished results (1994).