Organophosphorus Compounds, 119[◇]

The Phosphaalkyne Cyclotetramer System – Syntheses, Valence Isomerizations, and Reactions

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In contrast to their all-carbon analogues, phosphaalkyne cyclooligomers only became accessible a few years ago. A milestone in the chemistry of cyclotetramers was the synthesis and structural characterization of the tetraphosphacubane **5**, obtained as a thermolysis product of *tert*-butylphosphaacetylene (**1**). Since then, the construction of eleven cyclotetramers has been achieved, covering seven different frameworks (**A**–**G**). As a consequence of the use of kinetically stabilized phosphaalkynes as starting materials, all known cyclotetramers bear sterically demanding substituents (*tert*-butyl, *tert*-pentyl, 1-adamantyl). Cyclotetramerizations are not only achieved by thermolysis of **1**, but also by alternative and selective routes such as transition-metal-mediated, Lewis acid- and base-induced processes, as well as by cycloadditions to phosphaalkyne cyclotrimers. Interestingly, these tetramers can be interconverted by various valence isomerizations. The results of thermal and photochemically-induced rearrangements are in good agreement with MO calculations carried out for the parent compounds. Phosphaalkyne cyclotetramers exhibit a highly interesting reactivity and other peculiar features. One outstanding example is the tetraphosphacubane **5**, which shows unusual structural and spectroscopic properties as a result of its unique bonding arrangement.

[◇] Part 118: Ref.[1].

Manfred Regitz was born in 1935 in Saarland, studied chemistry at the Universities of Heidelberg and Saarbrücken and received his doctoral degree under the supervision of Professor Bernd Eistert on the subject "β-ketosulfones". After his habilitation in 1965 for research on diazo group transfer processes, he was appointed extraordinary professor in 1969 and then moved as full professor to the newly founded University of Kaiserslautern in 1971. Professor Regitz has accepted guest professorships in Aarhus (Denmark), San Jose (IBM, California), Rennes, Toulouse, Palaiseau (Ecole Polytechnique), and Metz (France) and Oviedo (Spain). He is the author of almost 400 papers on diazoalkanes, electrophilic and nucleophilic carbenes, antiaromatics, and low-coordinated compounds of phosphorus, in particular the phosphaalkynes. He is also author and editor of three monographs on diazoalkanes and low-coordinated phosphorus compounds. He is honorary professor of the University of Saarbrücken, has received the Alexander von Humboldt prize from the French Government, and is a member of the "Deutsche Akademie der Naturforscher Leopoldina" in Halle. At present, Manfred Regitz is editor of the international journal "Synthesis" and the renowned chemistry lexicon "Römpp", and coeditor of the standard reference work "Houben-Weyl, Methoden der Organischen Chemie". He is currently participating in the preparation of a successor to the latter, called "Science of Synthesis", which is scheduled for publication from 1999 onwards.

Andreas Mack was born in 1970 in Rheinland-Pfalz and started to read chemistry at the University of Kaiserslautern in 1990. For his preliminary diploma examination in 1992 he received the "Procter & Gamble Förderpreis", and during the summer of 1994 he was employed as a project manager at Procter & Gamble in Newcastle-upon-Tyne, England. In 1995, he received the "Steinhofer Prize" from the Adolf-Steinhofer-Stiftung for his diploma thesis entitled "Novel Phosphaalkyne Cyclotetramer Chemistry", prepared in Professor Regitz's laboratories. Since then, Andreas Mack has presented lectures at several congresses including "New Aspects in the Chemistry of Reactive Intermediates", held in Tsukuba, Japan. Since January 1996 his work has been supported by a postgraduate grant from the Fonds der Chemischen Industrie. His doctoral thesis under the supervision of Manfred Regitz on phosphaalkyne cyclooligomers and, in particular, trapping reactions of the highly reactive diphosphacyclobutadienes that occur as intermediates, will probably be completed in the spring of 1998.

MICROREVIEWS: This feature introduces Berichte's readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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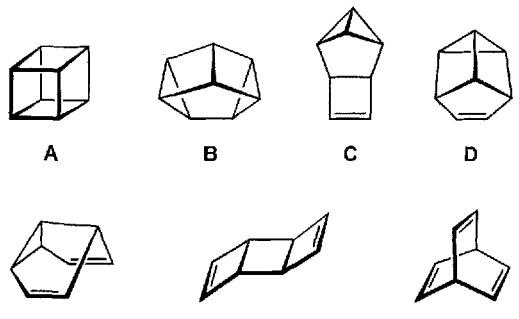
Introduction

Polycyclic cage compounds have long been a subject of interest and fascination for chemists. In this context, oligomeric species of compounds containing triple bonds, such as alkynes or heteroalkynes, are of great interest.

The chemistry of alkyne oligomers dates back to the 19th century and the work of Berthelot[2] and Kekulé[3]. The occurrence of tetramers in the cyclooligomerization of alkynes is a topic of particular interest, as it is in the series of phosphaalkynes (R−C≡P) as a consequence of the isolobal principle: the formal substitution of the HC or RC units of alkynes by valency isoelectronic phosphorus(III) moieties.

The history of alkyne cyclotetramers began in the second half of the 20th century[4]. Of the 17 (including stereoisomers: 22) possible frameworks in the $(CH)_8$ family, 14 have been synthesized to date[4d].

In addition to the numerous phosphaalkyne dimer complexes and the recent successful syntheses of free, stable trimers, the chemistry of phosphaacetylene tetramers is one area that has undergone the most tremendous development in the past few years. The foundation for the construction of these cyclooligomers was the synthesis of the first kinetically stabilized phosphaalkyne [*tert*-butylphosphaacetylene, (**1**)] by Becker in 1981[5] and the generalization and optimization of this process by Regitz in 1986[16]. Only three years later, the highly symmetrical tetraphosphacubane **5** was first synthesized, representing the first phosphaalkyne cyclotetramer (see Section 1.1). To date, the syntheses of 11 different tetramers covering 7 of 17 possible frameworks (**A**−**G**) have been reported.



To emphasize the actuality of this field of research, it should be mentioned that the preparations of ten phosphaalkyne cyclotetramers have been published in the last three years. An unfortunate consequence of such a rapid expansion in an area of interest to many chemists is the rather fragmentary nature of the work. Therefore, we have decided to summarize this topic in the present microreview, which is divided into three main parts: the first part deals with the different synthetic routes to phosphaalkyne tetramers; the second part covers the link between valence isomerizations and high-level ab initio MO calculations of the relative energies of these compounds. It will be shown that preparative and computational chemistry complement each other, leading to a better understanding of the rearrangements in question. Finally, the potential of phosphaacetylene tetramers for functionalization reactions is discussed in the third part (Section 3).

At present, each of the known phosphaalkyne cyclotetramers bears sterically demanding substituents, as a direct consequence of the use of kinetically stabilized phosphaalkynes as starting materials. All but one of the known tetrameric structures stem from *tert*-butylphosphaacetylene (**1**), the phosphaalkyne of choice with regard to synthetic work (best synthesis, isolation, handling, combined with high yield)[7]. Despite the fact that many of the mentioned cyclotetramers have also been synthesized as 1,1-dimethylpropyl (*tert*-pentyl), 1-adamantyl (1-Ad), or similar derivatives, we will concentrate on *tert*-butyl substitution and only comment on other substituents in cases of significantly differing reactivity.

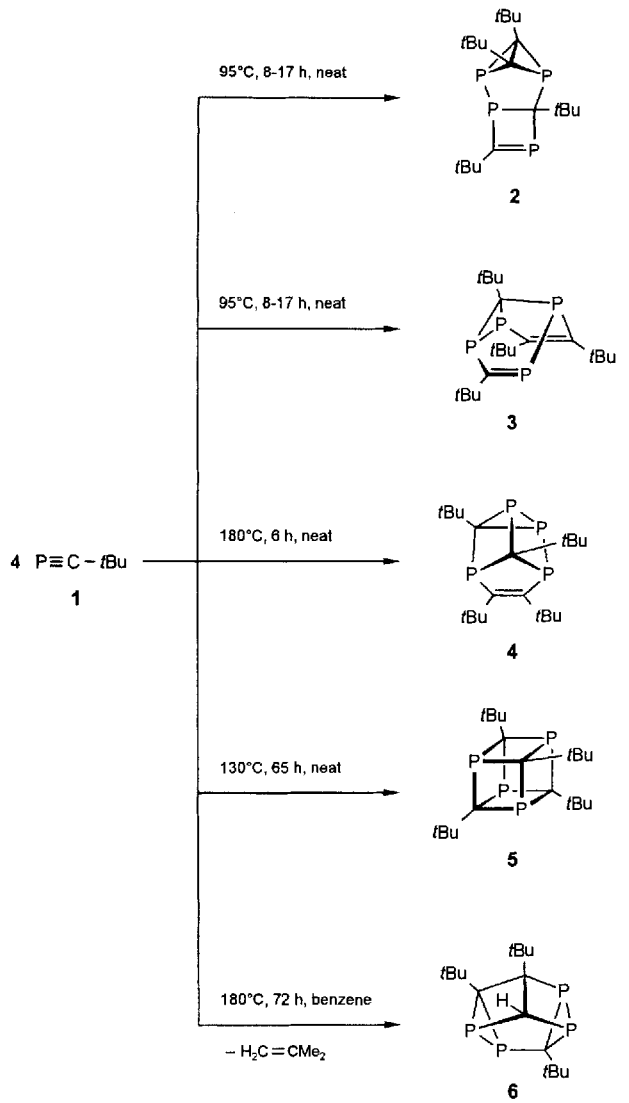
1. Synthesis of Phosphaalkyne Tetramers

In most cases, the construction of phosphaacetylene tetramers is characterized by direct, mostly one- or two-step procedures, in marked contrast to the difficult synthesis of alkyne tetramers, i.e. the multistep cubane (**A**) synthesis reported more than 30 years ago[8]. Without doubt, the thermolysis of *tert*-butylphosphaacetylene (**1**) represents the origin of phosphaacetylene tetramerization. More recently, the discovery of alternative routes has led to the synthesis of new skeletons and/or to better yields. In this respect, metal-mediated processes (see Section 1.2.) are responsible for the major progress in this highly interesting field of research.

1.1. Tetramers from Thermolysis of Phosphaalkynes

In spite of their sterically demanding substituents, kinetically stabilized phosphaacetylenes exhibit an enormous potential for cycloaddition reactions[7,9]. Surprisingly, thermolysis of *tert*-butylphosphaacetylene (**1**) leads to five different tetrameric structures.

The distribution of the products obtained can be controlled by altering the reaction temperature and is also dependent on the solvent. When *tert*-butylphosphaacetylene (**1**) is heated at 95°C for 8 h a complex mixture of products (ca. 5% yield) is formed, consisting of the tetracyclic compound **2**, the tetraphosphasemibullvalene **3**, and the tetraphosphabishomoprismane **4**[10]. The major product is the tetramer **2**; the ratio **2/3/4** being approximately 55:25:20. Extending the reaction time to 17 h leads to a different product ratio, with the tetraphosphatetracyclic compound **4** being favored (**2/3/4** ca. 20:35:45, 8% overall yield), this being − in agreement with MO calculations for the parent compound − the thermodynamically most stable phosphaalkyne tetramer (see Section 2). Even at higher temperatures (130−180°C) − again in the absence of a solvent − the tetraphosphacubane **5** and the tetraphosphabishomoprismane **4** are formed. The optimized conditions giving the best selectivity are 130°C/65 h for **5** (8%)[11] and 180°C/6 h for **4** (7%)[12]. Both tetramers can be isolated and purified by bulb-to-bulb distillation. It is worthy of note that the cubane **5** as well as the bishomoprismane **4** can also be prepared by specific processes (see below). Last but not least, the tetraphosphacuneane **6** is obtained at a comparable



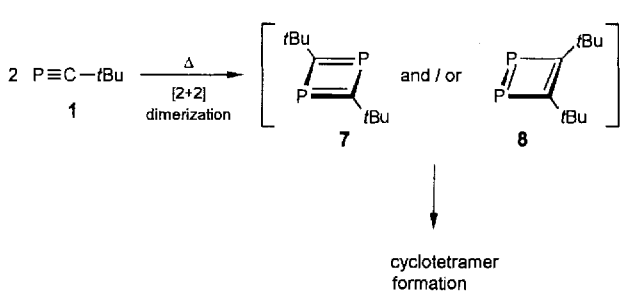
temperature but in the presence of a solvent[9]. Remarkably, **6** does not represent a true tetramer of **1** since one *tert*-butyl substituent is removed as isobutene in the course of its formation.

The constitutions of the tetracyclic compound **2** and the cuneane **6** have been elucidated unequivocally by analytical and spectroscopic methods. The cage skeletons of the semibullvalene **3** and the bishomoprismane **4** were determined by single-crystal structure analyses of their mesitylnitrile oxide cycloadduct **52** and bis(pentacarbonyltungsten) complex **50**, respectively (see Section 3). The constitution of the highly symmetrical tetraphosphacubane **5** itself was demonstrated by an X-ray structure analysis. Undoubtedly, the latter compound and the tetraphosphasemibullvalene **3** constitute the most interesting examples of the phosphaalkyne tetramers.

The tetraphosphacubane **5** shows interesting structural and spectroscopic properties, which are worthy of more detailed discussion. Single-crystal X-ray analysis[11] reveals a distorted cubic structure with identical P–C bond lengths [1.881(3) Å]. As might be expected, the interior angles are, respectively, smaller [C–P–C = 85.6(1)°] and larger [P–C–P = 94.4(2)°] than those of cubane itself. Hence, the pentacyclic compound **5** has a remarkably low ring-strain energy of ca. 63 kcal·mol^{-1}[13], which is more than 100 kcal·mol^{-1} less than that of cubane[14]. This amazingly reduced ring strain in **5** can be attributed to two factors: (1) the ability of phosphorus to accommodate small angles, thus allowing the angles at carbon to exceed 90°, and (2) the high ionic character of the P–C bonds, which results in a stable electrostatic environment. As expected, in the ^{13}C- and ^{31}P-NMR spectra the respective atoms give rise to only one signal each, but the chemical shifts of the skeletal carbon and phosphorus atoms of $\delta = -29.1$ and $\delta = +257.4$, respectively, were initially somewhat difficult to interpret in terms of established concepts. However, photoelectron spectroscopic (PE) investigations[15] revealed an effective participation of the lone electron pairs at phosphorus in the σ(P–C) bonds of the cube via electron transfer, giving rise to a partial positive charge at phosphorus and a partial negative charge at carbon. Moreover, the calculated[15] net charges are in accord with the PE studies. As will be mentioned below, the unusual bonding situation in **5** naturally has a significant influence on the basicity (nucleophilicity) of the phosphorus atoms (see Section 3.1.). It is worth mentioning that the gas-phase basicity has been measured by FT-ICR spectroscopy, revealing that **5** is a rather strong base in the gas phase, since it was found to be about 26 kcal·mol^{-1} more basic than ammonia. Additionally, molecular orbital studies show that the unsubstituted parent compound and the tetramethyl-substituted derivative are carbon-bases rather than phosphorus-bases in the gas phase[16].

In the case of the tetraphosphasemibullvalene **3**, NMR-spectroscopic studies do not reveal any dynamic structural interconversion at room temperature[10], in contrast to its all-carbon analogue **E**[17]. NMR experiments at elevated temperature are not possible because **3** rearranges to **4** upon heating[10].

As far as the reaction mechanisms are concerned, the obtained product distribution allows the assumption of both head-to-head and head-to-tail [2 + 2]-dimerizations as the initial reaction steps, resulting in the generation of 1,3- (**7**) and 1,2-diphosphacyclobutadienes (**8**)[11,18]. However, it has not yet been possible to detect any intermediates in the cyclotetramerization process. Nevertheless, trapping reactions of 1,3-diphosphacyclobutadienes (**7**) with phosphaalkynes, alkynes, and alkenes have recently been realized (see Section 1.2.1.).

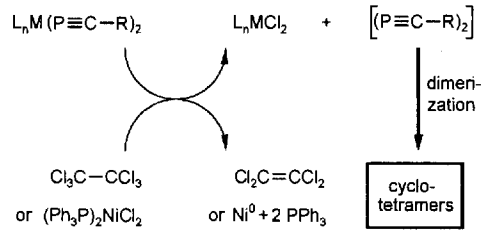


1.2. Tetramers from Metal Template Stabilized Phosphaalkyne Cyclooligomers

Cyclooligomerization processes in the coordination sphere of a metal have provided the basis for major advances in the chemistry of phosphaalkyne tetramers. Thus, cyclodimerization[19], cyclotrimerization[20], and, just recently, cyclotetramerization[21] processes have been realized, which yield the corresponding metal complexes. Moreover, subsequent liberation of the organophosphorus ligand has been successful in most cases. This enables the preparative chemist to use the oligomeric phosphaalkyne unit as a versatile building block in the synthesis of phosphorus-carbon cage compounds, especially tetramers.

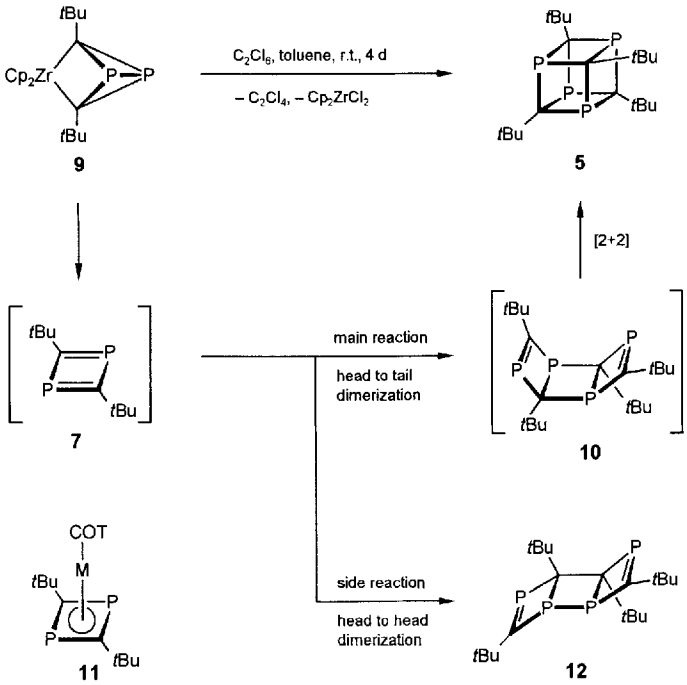
1.2.1. Tetramers from Transition-Metal–Phosphaalkyne-Dimer Complexes

As mentioned above, division of the cyclotetramerization into two cyclodimerization steps proved to be a highly advantageous route for the synthesis of the tetraphosphacubane **5** and the tetraphosphatricyclooctadienes **12** and **13**[22]. Accordingly, the first step of the procedure is the synthesis of early transition-metal–phosphaalkyne-dimer complexes of the types **9**[19g], **11**[20b], and **15**[19f], which are now readily accessible. In the final step, an oxidizing agent removes the metal fragment. The liberated phosphaacetylene-dimer intermediates themselves then undergo dimerization processes to furnish the tetramers.



On the one hand, it is mandatory that the oxidizing reagent cleaves the metal fragment by transforming the latter into thermodynamically stable compounds such as L_nMCl_2. On the other hand, the entire – or parts of the – auxiliary agent itself may not be incorporated into the final product. Mild chlorinating reagents such as hexachloroethane or bis(triphenylphosphane)nickel dichloride were found to fulfil these requirements perfectly[22]. Hexachloroethane is reduced to tetrachloroethene, which can be removed easily (25°C/10^{-3} mbar) during the course of the reaction, whereas the nickel compound simultaneously forms elemental nickel and triphenylphosphane while chlorinating the transition-metal–phosphaalkyne-dimer complexes.

This key discovery provides the means for the selective liberation of phosphaalkyne-dimeric species, which then undergo consecutive dimerizations to furnish the desired tetramers:

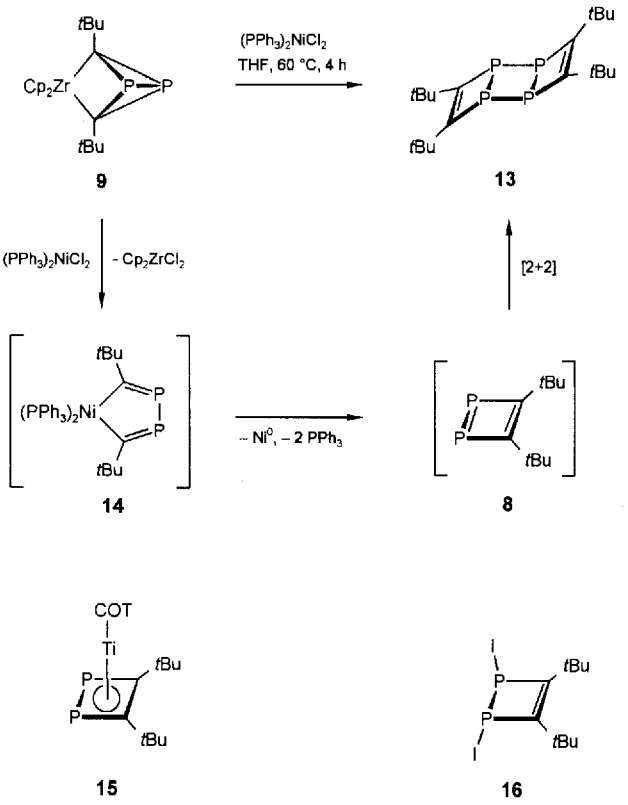


Thus, starting from the tricyclic zirconocene complex **9**, the tetraphosphacubane **5** is isolated in high yield (70%) using hexachloroethane as a chlorinating reagent. In this way, tetraphosphacubanes bearing other bulky substituents such as *tert*-pentyl (80%), methylcyclopentyl (60%), and methylcyclohexyl (50%) are accessible in good to high yields. The 1-adamantyl group is an exception; in this case the yield is lower (30%) due to the simultaneous formation of valence isomers (see below)[12,22a]. Moreover, the pentacyclic tetramer **5** can also be isolated (34%) when the η^4-1,3-diphosphacyclobutadiene complexes **11** of zirconium[23] and hafnium[20b] are treated with hexachloroethane.

From a mechanistic point of view, dimerization of the liberated 1,3-diphosphacyclobutadiene **7** via a head-to-head or a head-to-tail orientation seems to be plausible. The latter is more probable due to steric hindrance of the bulky substituents in the transition states of the [4 + 2] cyclodimerization of **7**. A final [2 + 2] dimerization of the *cis*-tetraphosphatricyclooctadiene intermediate **10** completes the reaction sequence. The intermediacy of **7** is strongly supported by the presence of traces (<5%) of the head-to-head dimerization product **12**, which has been fully characterized, notably by a crystal structure determination[22b]. Further indications for the involvement of 1,3-diphosphacyclobutadienes as reactive intermediates have been reported in the literature[12,22a] and are supported by our own investigations[24]: When the tricylic zirconocene–phosphaalkyne-dimer complex **9** is treated with hexachloroethane in the presence of a trapping reagent such as a phosphaalkyne or an olefin the formation of cyclotetramers is not observed. Instead, the dimeric phosphaalkyne intermediate is trapped completely. The observed range of products most likely stems from cycloaddition reactions of 1,3-diphosphacyclobutadiene intermediates (**7**). In this manner,

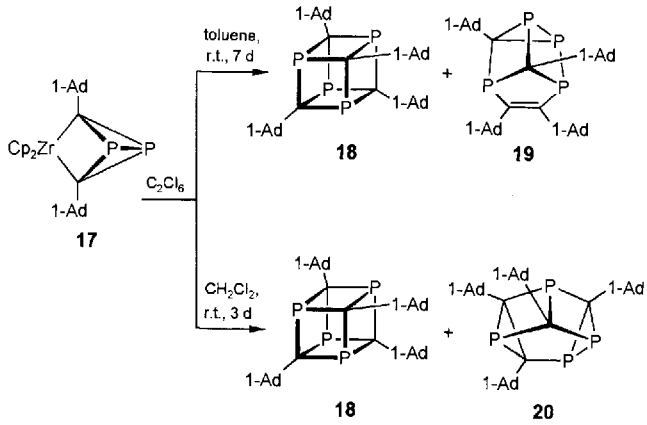
new polycyclic compounds such as a variety of 2,5-diphosphabenzvalenes, 1,3-diphospha-Dewar benzenes and 1,3-diphospha-4,5-dihydro-Dewar benzenes are accessible[24].

Another phosphaalkyne cyclotetramer (**13**) with a tricyclooctadiene skeleton (**F**), but with a different distribution of P- and *t*Bu–C- units is obtained from the tricyclic zirconium complex **9** when hexachloroethane is replaced by bis(triphenylphosphane)nickel dichloride. This clean reaction leads to the specific formation of the tetramer **13**, which can be isolated in 70% yield and has been fully characterized by several techniques, including single-crystal diffraction analysis, which revealed a planar, rectangular P_4 unit[22b].



Mechanistically, the formation of the cyclotetramer **13** can be rationalized in terms of an initial replacement of the zirconocene fragment by the bis(phosphane)nickel unit. Subsequent cleavage of two P–C bonds leads to the nickelladiphosphacyclopentadiene intermediate **14**, which spontaneously loses nickel(0) and triphenylphosphane (both isolated) to liberate the 1,2-diphosphacyclobutadiene intermediate **8**. A final [2 + 2] dimerization in a head-to-head orientation selectively furnishes the tricyclic compound **13**[22b]. Further support of the intermediacy of **8** is provided by two alternative and independent reactions. Firstly, the same tricyclic tetramer **13** is produced selectively by treating the cyclooctatetraene titanium complex **15** (bearing a preformed 1,2-diphosphacyclobutadiene unit) with hexachloroethane or, secondly, by allowing the diiodophosphacyclobutene **16**[25] to react with $[(PPh_3)_2Pt(C_2H_4)]$[19f].

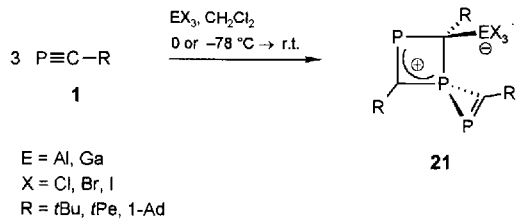
As a sole but surprising exception, the metal extrusion from the 1-adamantyl derivative **17** does not proceed selectively and is solvent-dependent[9,12]: In toluene, the tetraphosphabishomoprismane **19** is formed together with an equal amount of **18** (30%). The use of dichloromethane as a more polar solvent under otherwise identical reaction conditions gives rise to the formation of **18** (25%) together with the tetraphosphacuneane **20** (30%). An X-ray structure determination revealed the framework of **20** to be isomeric with that of **6**[26]. As yet, we have been unable to provide a convincing explanation for the different reaction pathways.



1.2.2. Tetramers from Metal–Phosphaalkyne-Trimer Complexes and Free Trimers

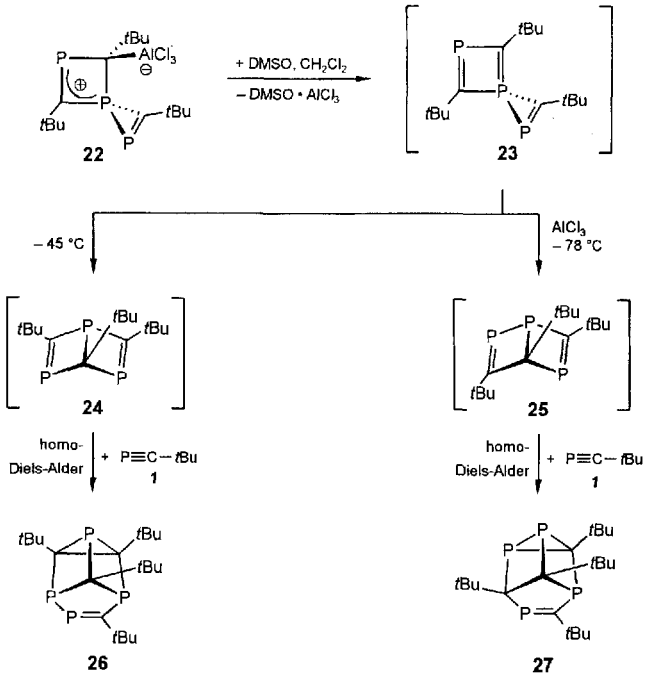
1.2.2.1. Tetramers with the Aid of Lewis Acids

Aluminium phosphaalkyne-trimer complexes of the type **21** show parallels to the above-mentioned transition-metal–phosphaalkyne-dimer complexes since the metal unit can easily be removed. The construction of the desired tetramers again involves two reaction steps. Firstly, aluminium trihalides or gallium trichloride are allowed to react with three equivalents of a kinetically stabilized phosphaalkyne to provide the betaines **21** in an unusual spirocyclotrimerization process[27].



In the second step, the original Lewis acid is removed, which can be achieved even by treatment with the weak Lewis base dimethyl sulfoxide. Starting from the *tert*-butyl/$AlCl_3$ derivative **22**, the subsequent reactions proceed selectively to furnish two new tetramers (**26** and **27**). A plausible reaction mechanism involves an initial liberation of the spirocyclic trimer **23**, which cannot itself be isolated. However, addition of a further equivalent of *tert*-butylphosphaacetylene (**1**) to the reaction mixture prior to the generation of **23** leads – depending on the reaction conditions – to the

formation of two constitutional isomers, the tetraphosphabishomoprismanes **26** and **27**[27]. Both valence isomers show the structural characteristics of a P/C double bond bridging the prism, in contrast to the aforementioned third isomer **4** (C=C bridge). The constitutions of the tetracyclic cage compounds **26** and **27** have been unambiguously derived from analytical and spectroscopic data. An X-ray structure analysis of the [3 + 2] cycloadduct of **27** with mesitylnitrile oxide additionally proved the proposed cage skeleton (see Section 3.4)[27].



22 **23** **24** **25** **26** **27**

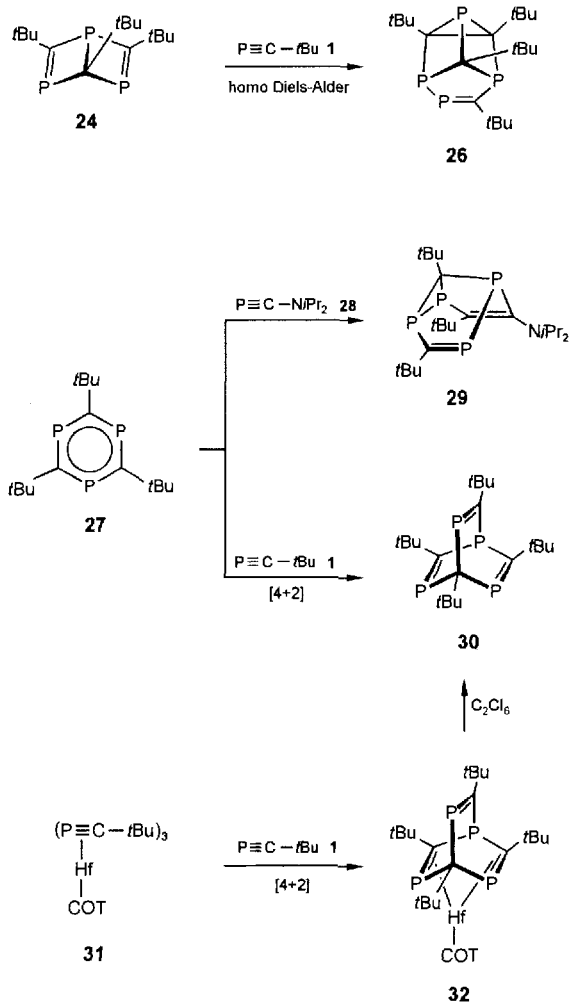
The reaction most likely proceeds via triphospha-Dewar benzenes **24** and **25** as intermediates and ends with regiospecific homo-Diels-Alder reactions. Recent investigations give further evidence in support of this mechanism (see below).

1.2.2.2. Tetramers from Free Trimers and Transition Metal Template Stabilized Trimers

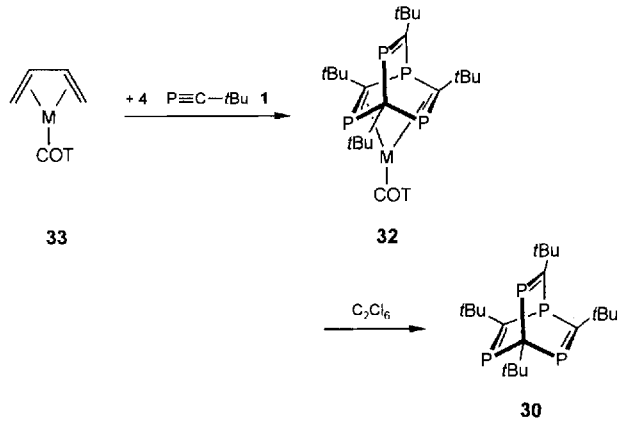
The existence of triphospha-Dewar benzenes as key intermediates in the formation of the above-mentioned tetramers **26** and **27** is supported by independent investigations of Binger et al.: Recently, the first isolation of the bicyclic trimer **24**, via a transition-metal-mediated reaction sequence was reported[20b]. The reasonably stable 1,3,5-triphospha-Dewar benzene **24** undergoes clean, regiospecific homo-Diels-Alder reactions with various phosphaalkynes and even with alkynes, leading to new tetramers of the type **26** with 3:1 substitution patterns (R ≠ *t*Bu) and new triphosphabishomoprismanes, respectively[28].

The renaissance of phosphaalkyne oligomers is also reflected in the successful synthesis, isolation, and crystal structure analysis of the first triphosphabenzene **27**[20b]. The surprising reaction of the planar, aromatic 1,3,5-triphosphinine **27** with the amino-substituted phosphaalkyne **28**[29] leads to the formation of the tetraphosphasemibullvalene **29**, which contains the same cage skeleton as **3** (see above)[30]. In contrast, a clean [4 + 2] cycloaddition of **27** with *tert*-butylphosphaacetylene (**1**) furnishes the expected tetraphosphabarrelene **30** (98%)[30], a phosphaacetylene cyclotetramer that has been previously synthesized by a unique tetramerization at a transition metal center (see Section 1.2.3.).

Tetraphosphabarrelenes **30** are also obtained by a stepwise procedure starting from cyclooctatetraene hafnium–phoshaalkyne-trimer complexes {**31**, COT = η^8-C_8H_8, η^8-C_8H_6[1,3-$(SiMe_3)_2$]}. Cycloaddition of these complexes, which have not been fully structurally characterized, with a further equivalent of phosphaalkyne **1** gives rise to the barrelene complexes **32**[23,28]. The "magic" hexachloroethane is again very effective in liberating the organophosphorus ligand. It is worthy of note that the synthesis of tetramers with 3:1 substitution patterns can be achieved starting from isolated trimeric species (**24**, **27**, **31**) and different phosphaalkynes (R–C≡P, R = *t*Pe, 1-Ad, instead of *t*Bu)[28,30].



24 **26** **29** **27** **30** **31** **32**

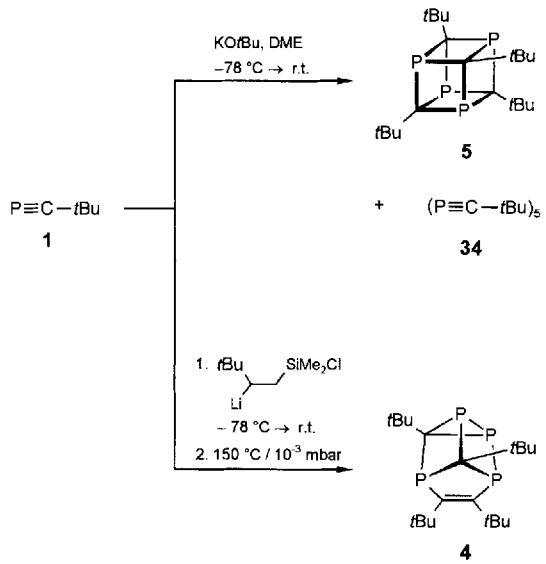


1.2.3. Direct Tetramerization at Transition Metal Fragments

As already mentioned, tetraphosphabarrelenes are easily constructed starting from isolated trimers or trimer complexes, but these routes only have a substantial benefit when 3:1 substitution patterns are desired. However, the original synthesis represents the first direct tetramerization of a phosphaalkyne at a metal fragment. Treatment of the cyclooctatetraenezirconium– or -hafnium–butadiene complexes (type **33**) with a least four equivalents of *tert*-butylphosphaacetylene (**1**) selectively furnishes barrelene complexes of the type **32**[20b,21] in high yields (M = Zr: 81%). Removal of the metal fragment leads exclusively to the tetraphosphabicyclooctatriene **30** (M = Zr: 88%), the first tetramer containing three phosphaalkane subunits. The structure of the latter product has also been determined by X-ray analysis, confirming the postulated symmetrical arrangement[20b].

1.3. Base-Induced Tetramerization

It is known from acetylene chemistry that not only (Lewis) acids but also bases are capable of inducing oligo- and polymerization reactions. To a certain extent, this principle can also be applied to phosphaalkyne chemistry.



When *tert*-butylphosphaacetylene **1** is allowed to react with potassium *tert*-butoxide, the tetraphosphacubane **5** is formed in 20% yield. As a side product, 4% of the previously known pentamer **34**[31] is also isolated[27a]. Replacement of potassium *tert*-butoxide by the stronger base chlorodimethyl(3,3-dimethyl-2-lithiobutyl)silane leads selectively to the previously reported bishomoprismane **4**, which can be isolated in the highest yield (20%) by this route as compared to all others routes[27a].

In analogy to the thermolysis of phosphaalkynes, bases also predominantly induce the formation of tetramers, whereas metals (transition metal fragments and main group Lewis acids) lead mainly to di- and trimerizations, with the sole exception of the direct tetramerization to the barrelene complex **32**.

1.4. Tetramers by Valence Isomerizations from Other Tetramers

Recently, interconversions of phosphaalkyne tetramers have been reported[10]. Although these valence isomerizations have not yet led to new frameworks in the $(P{\equiv}CR)_4$ series, some of these reactions represent the best yielding accesses to particular tetramers, especially for the formation of derivatives with *tert*-pentyl substitution. For methodological reasons this topic is explained in detail in a separate section (Section 2).

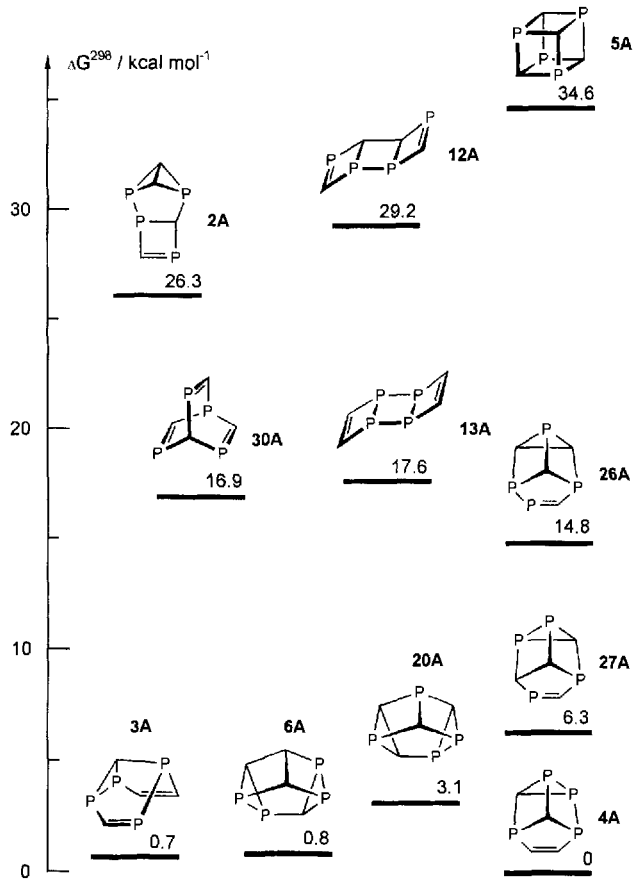
2. Valence Isomerization Reactions of Phosphaalkyne Tetramers – The Link Between Preparative and Computational Chemistry

Interconversions of alkyne oligomers by means of thermally- and photochemically-induced valence isomerizations play an important role in all-carbon chemistry, especially in the $(CH)_8$-family, and have been known for more than 40 years[4]. Recently, isomerization reactions have also been realized within the phosphaalkyne tetramer system, the likes of which have not previously been reported in the chemistry of phosphorus-carbon cage compounds[10]. The rearrangements in the $(P{\equiv}CR)_4$ series are of great mechanistic and theoretical interest and show both similar and differing results when compared to the chemistry of alkyne tetramers.

In the last 20 years, so-called computational chemistry has developed to such a great extent that even preparative chemists nowadays use high-level ab initio MO calculations. Not infrequently, the theory offers an in depth understanding of reactions and sometimes even leads to excellent predictions. With regard to phosphaalkyne cyclotetramers, the relative energies, transition states for their formation, and even IGLO ^{31}P-NMR chemical shifts have recently been calculated for the parent compounds[22b][32]. The relative energies (as calculated for the parent compounds, R = H) and the valence isomerizations of the tetramers are shown in Figure 1 and in the following formulae.

First of all it should be mentioned that all phosphaacetylene cyclotetramers are thermodynamically much more favored than the parent monomers (P≡CH, 107 kcal/mol) or two dimers (1,2-diphosphete (**8**): 93 kcal/mol; 1,3-diphosphete (**7**): 111 kcal/mol; diphosphatetrahedrane: 78 kcal/mol)[22b]. With regard to the order and the energy values of the tetramers, the parent tetraphosphacubane **5A**

Figure 1. Relative energies of $(HCP)_4$ isomers calculated by high-level ab inito methods[22b,32]

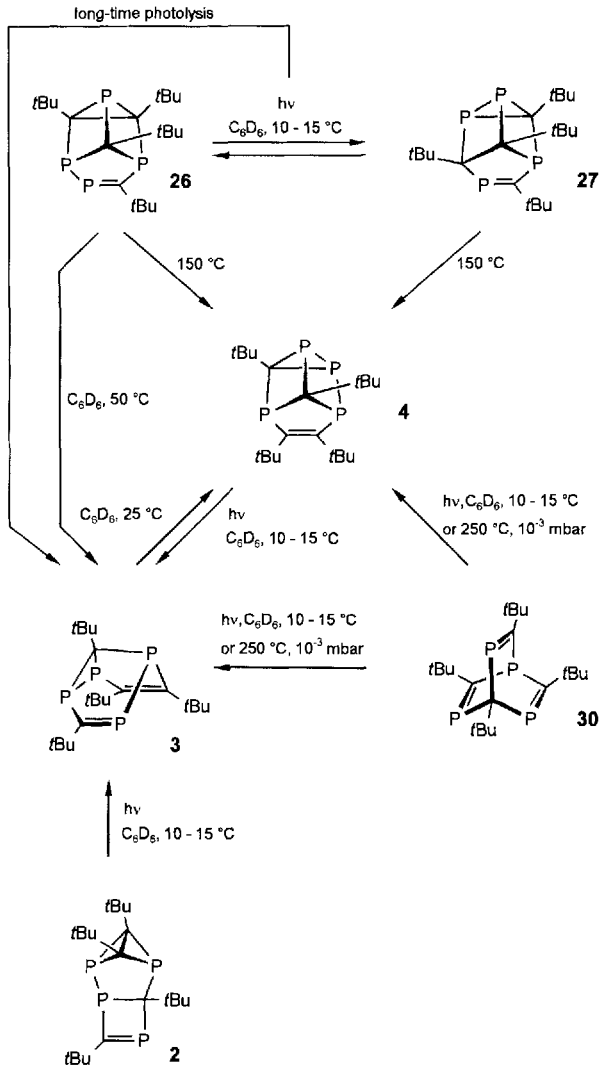


surprisingly represents the thermodynamically less favored skeleton, as is the case for the $(CH)_8$-cubane **A**[4,32]. The observed high stability of the *tert*-butyl derivative **5** (i.e., melting point without decomposition at 241 °C) must therefore be due to kinetic aspects. In contrast to all-carbon chemistry[4d], the cubane **5** and the tricyclooctadiene **13** do not take part in any valence isomerization process. No such studies have yet been carried out for the isomers **12** and the two cuneanes **6** and **20**, which are very stable tetramers on the basis of calculations performed for the parent compounds **6A** (0.8 kcal/mol) and **20A** (3.1 kcal/mol). The remaining six phosphaalkyne cyclotetramers are all involved in a complex valence isomerization system.

Clearly, the bishomoprismane **4** is the thermodynamically most favored tetramer, which is in perfect agreement with the calculations for the parent compound **4A** (zero point): **4** is formed when the isomeric bishomoprismanes **26** (48%) and **27** (100%), the semibullvalene **3** (20% after 7 days at 25 °C; 100%, 2 h, 150 °C)[10], as well as the barrelene **30**[23] are heated individually. The bishomoprismane **4** is 6.3 kcal/mol lower in energy than the constitutional isomer **27** and shows an even larger difference of 14.8 kcal/mol relative to **26**. A further indication of the expected low stability of the latter is that it undergoes thermal rearrangement to the semibullvalene **3** under milder conditions (50 °C). In this case a mixture of **3** and **4** is obtained since **3** itself slowly rearranges to **4**.

The tetraphosphasemibullvalene **3A** is second lowest in energy, albeit only 0.7 kcal/mol higher than **4A**. The all-carbon analogue of **3A** (**E**) is the thermodynamically most stable tetramer[4].

The tetracyclic tetramer **2A** is around 26 kcal/mol higher in energy than **3A** and **4A**. Although the thermolysis of **2** has not yet been reported, it can be expected to rearrange into the thermodynamically more favorable isomers **3** and **4**. One piece of evidence in support of this assumption is that the thermolysis of *tert*-butylphosphaalkyne (**1**) for longer periods leads to higher amounts of semibullvalene **3** and bishomoprismane **4** with a concomitant decrease in the yield of the tetraphosphatetracyclooctene **2** (see Section 1.1).



In the $(P{\equiv}CR)_4$ series, the tricyclic compound **3** exhibits the photochemically most favored cage structure: All five cyclotetramers incorporated in this valence isomer system (**2**, **4**, **26**, **27**, and **30**) rearrange to the tetraphosphasemibullvalene **3** upon irradiation at wavelengths longer than 280 nm[10]. It should first be mentioned that the two isomeric tetracyclic compounds **26** and **27** establish a 1:1

photochemical equilibrium. Long-term irradiation of these two isomers leads to the expected tetraphosphasemibullvalene **3**[27a]. A 75% conversion of the tetraphosphabishomoprismane **4** to **3** is also achieved by photolysis in solution. Moreover, the tetracyclic tetramer **2** completely rearranges upon photolysis, forming the semibullvalene **3** (80%) and the bishomoprismane **4** (20%). The occurrence of **4** most likely stems from the already-mentioned spontaneous thermal isomerization of **3**[10]. Finally, it is worthy of note that the photochemical behavior of the tetraphosphabarrelene **30** is very similar to that of the tetracyclic compound **2**[23].

On comparing these results with isomerizations of alkyne tetramers, it is apparent that the semibullvalene **E** is indeed formed by irradiation of bishomoprismane (**D**) and barrelene (**G**) but, in contrast to the phosphaalkyne tetramer system, the presence of a triplet sensitizer is necessary[4d]. Moreover, direct photolysis of tetracyclo[4.2.$0^{2,4}$.$0^{3,5}$]oct-7-ene (**C**) does not lead to the semibullvalene skeleton **E**, but rather to cyclooctatetraene[4d], for which no tetraphosphaanalogue is yet known.

Since it has not yet been possible to detect any intermediates, any comments on the mechanisms of the above-mentioned rearrangements must remain purely speculative. However, the observed valence isomerizations can be interpreted rather simply and convincingly in most cases and involve reaction steps known from valence isomerizations in all-carbon chemistry[27a].

3. Reactivity of Phosphaalkyne Tetramers

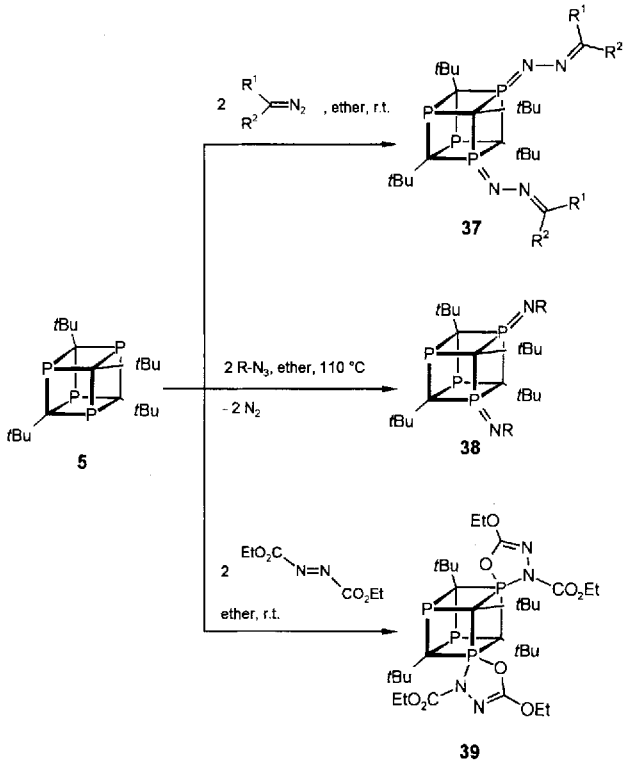
Apart from the synthesis of phosphaalkyne cyclotetramers, there is a particular interest in their reactivity as these polycyclic compounds contain not only double bonds, diene units, and strained single bonds, but also four phosphorus atoms that are predisposed to functionalization reactions. To date, derivatization reactions have been reported for six of eleven known phosphaalkyne tetramers (**3**, **4**, **5**, **13**, **27**, and **30**) and these are described in the following sections. As a consequence of its high-yield synthesis via the metal-mediated two-step process (Section 1.2.1.), the tetraphosphacubane **5** has been examined the most thoroughly.

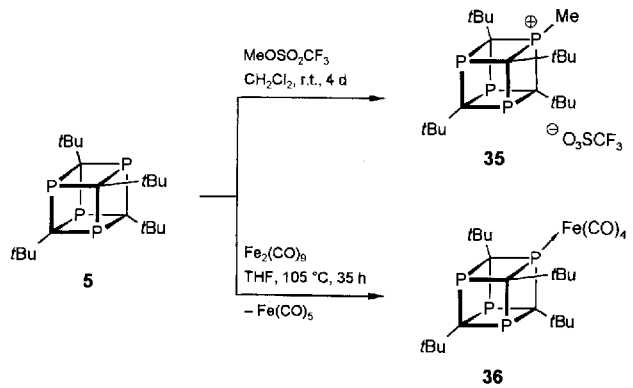
3.1. P-Functionalization of the Tetraphosphacubane (5)

As mentioned above (Section 1.1.), the strong participation of the lone pairs of the phosphorus atoms in the σ(P–C) framework bond significantly reduces the nucleophilicity of the heteroatoms. Therefore, particularly strongly electrophilic reagents are necessary for P-functionalization reactions on the tetraphosphacubane system.

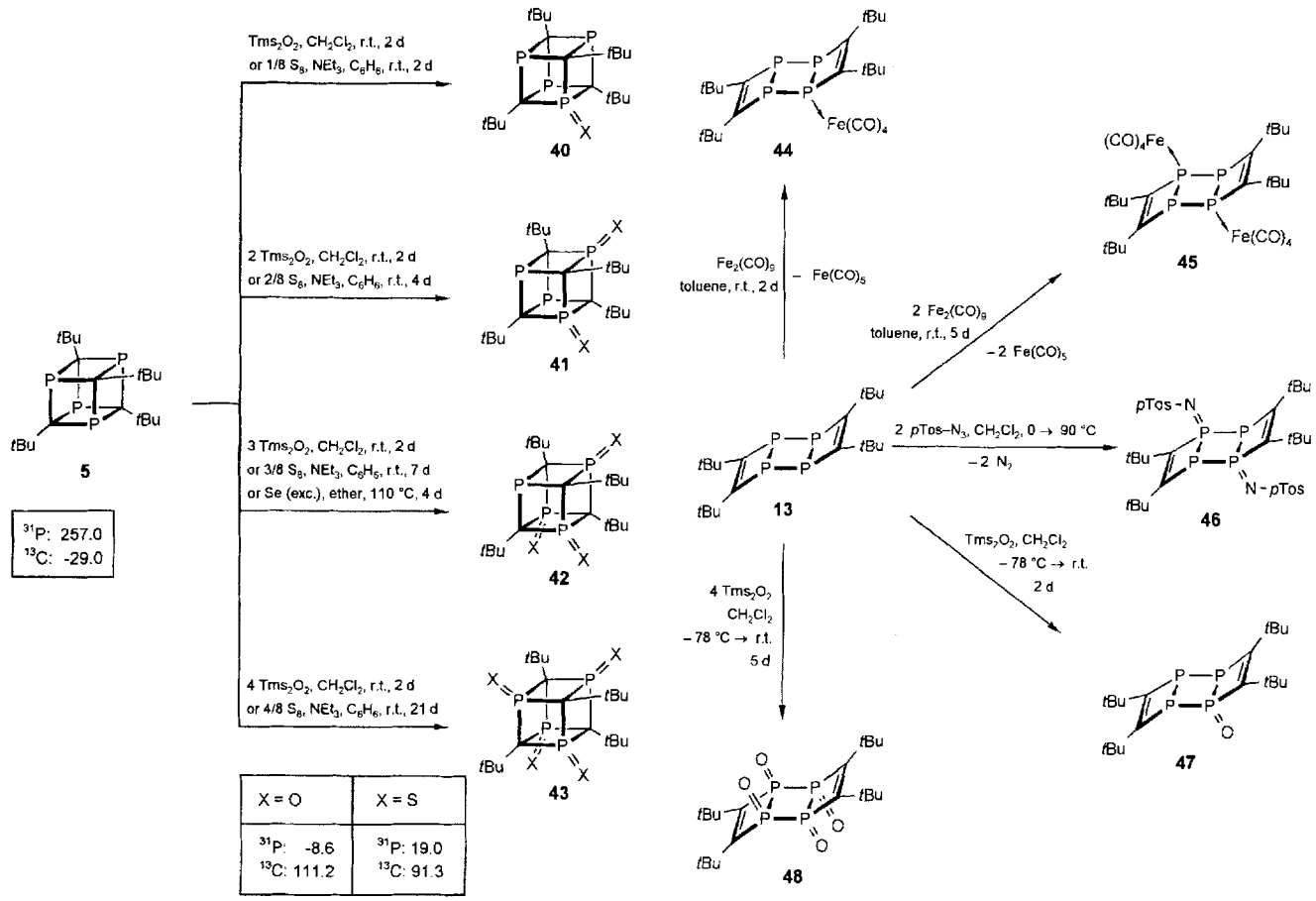
Hence, alkylation with methyl triflate (→ **35**, 95%) as well as complex formation with nonacarbonyldiiron (→ **36**, 56%) take place solely at one phosphorus atom, even in the presence of an excess of the respective reagent[33].

In spite of the reduced electron density at phosphorus in **5**, double P-functionalizations (in addition to the corresponding mono functionalizations) are possible with various diazoalkanes and azides leading to the bis(phosphazines) **37** (R^1 = *t*Bu, R^2 = H: 95%) and the double Staudinger products **38** (R = Me: 85%), respectively[33,34]. Moreover, **5** undergoes [4 + 1] cycloaddition reactions with two equivalents of electron-poor partners such as diethyl azodicarboxylate (affording the bis-adduct **39**, (75%)[34] and tetrachloro-*ortho*-benzoquinone)[33] (not shown). In no case does an excess of the reagent lead to further oxidative addition reactions.





The highest degree of functionalization at the tetraphosphacubane system **5** is achieved by the introduction of elements of Group 16: At room temperature, the stepwise addition of oxygen [using bis(trimethylsilyl) peroxide] and sulfur [under triethylamine catalysis] lead – depending on the stoichiometry – selectively to the respective mono-, di-, tri-, and tetraoxidized products **40**, **41**, **42**, and **43** (X = O, S)[35]. In contrast, a similar reaction with selenium affording the triselenide **42** (X = Se, confirmed by X-ray analysis)[33] is only observed on heating the tetraphosphacubane **5** with a large excess of selenium at 110 °C over a four-day period.



In the case of the tetra-chalcogenation products **43** (X = O, S), ^{31}P- and ^{13}C-NMR spectroscopy demonstrate the dramatic changes in the bonding situation among the cage atoms: The signal of the phosphorus atoms is shifted upfield from δ = +257.0 in **5** to −8.6 (X = O) or +19.0 (X = S), the latter values being appropriate for $\lambda^5\sigma^4$ phosphorus nuclei. At the same time, the carbon signals are drastically shifted downfield from δ = −29.0 (**5**) to +111.2 (X = O) or +91.3 (X = S), not only showing the normality of the situation, but also indicating the acceptor character of the P=X groups in **5**[35].

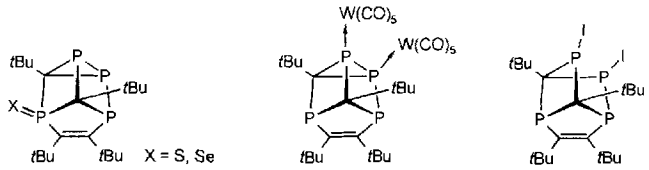
3.2. P-Functionalization of the Tetraphosphatricyclooctadiene (13)

In contrast to the aforementioned tetraphosphacubane **5**, no extreme positions of ^{31}P- and ^{13}C-NMR resonances are observed for the cyclotetramer **13**; this is also valid for its P-functionalized derivatives. In contrast to **36** (see above), not only one (→ **44**, 60%) but also two tetracarbonyliron fragments can be attached to the tricyclic compound **13** (→ **45**, 45%).

In analogy to **5**, mono- and double Staudinger products (→ **46**, 60%) are accessible when **13** is allowed to react with one or two equivalents of *p*-tosyl azide, respectively. Both controlled mono- and tetrachalcogenations have been realized, leading, for example, to the mono-oxygenated compound **47** (90%) and the per-oxygenated tetraphosphatricyclooctadiene **48** (55%)[26].

3.3. Reactivity of the Tetraphosphabishomoprismane (4)

In addition to the already described valence isomerizations, the tetracyclic phosphaalkyne cyclotetramer **4** undergoes various functionalization reactions: Interestingly, **4** shows differing reactivity towards chalcogens or transition metal fragments and halides. Whereas sulfurization and selenation take place exclusively at the non-phosphorus-substituted P-4 (→ **49**; X = S: 70%[12] and X = Se: 75%[27a]), the reaction with [W(CO)$_5$·thf] affords the bis(pentacarbonyltungsten) adduct **50** (32%).



49 **50** **51**

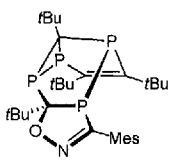
A single-crystal X-ray diffraction study revealed that the two metal fragments are attached to both phosphorus atoms of the diphosphirane unit[37]. Treatment of **4** with

iodine selectively leads to P–P bond cleavage of the diphosphirane subunit (→ **51**, 70%)[36]. Based on theoretical calculations on the parent compound **4A**, the differences in the ligating behavior of **4** towards S/Se and $W(CO)_5$ are assumed to reflect electronic as well as steric factors[37].

3.4. Reactivity of the Tetramers (3, 27, and 30)

No detailed reactivity studies on the phosphaalkyne cyclotetramers **3**, **27**, and **30** have as yet been carried out, although both cycloaddition and complexation reactions have been reported.

[3 + 2] Cycloadditions of mesitylnitrile oxide with the tetraphosphasemibullvalene **3** and the tetraphosphabishomoprismane **27** afford regio- and stereospecifically the tetracyclic system **52**[10] and the pentacyclic compound **53**[27], respectively. The constitutions and stereochemistries of both cycloadducts **52** and **53** were unambiguously confirmed by X-ray crystal structure analyses. The presence of the 1,4-diphospha-1,4-diene subunits in the tetraphosphabarrelene **30** is evident from a homo-Diels-Alder reaction with methyl propynoate, which results in formation of the tetracyclic product **54** (98%)[23].



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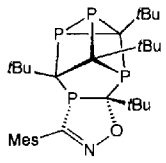

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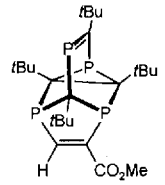

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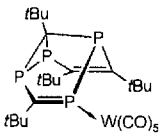

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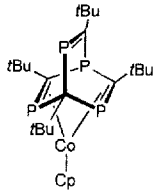

56

Two metal complexes of the tetramers **3** and **30** have recently been synthesized. The pentacarbonyltungsten fragment specifically coordinates to the $\lambda^3\sigma^2$ phosphorus of the tetraphosphasemibullvalene **3** with η^1-coordination (→ **55**, 69%), even when an excess of $W(CO)_5 \cdot$thf is used[10]. Finally, it should be mentioned that a $\eta^{2:2}$-ligated tetraphosphabarrelene (**56**, 48%) is accesible by treatment of **30** with cyclopentadienylbis(ethylene)cobalt at low temperatures. The structure of the cobalt complex **56** has been unambiguously determined by X-ray diffraction analysis[23].

Conclusions and Reflections

The synthesis of alkyne cyclotetramers often causes significant problems because, in most cases, difficult multistep and even low-yield procedures must be tolerated. Moreover, alkynes are very rarely appropriate starting materials for the construction of the respective tetramers. In contrast, the ease of preparation of numerous phosphaalkyne cyclotetramers is astonishing: The tetramerization processes predominantly consist of single- or two-step procedures when starting from kinetically stabilized phosphaalkynes. For example, simple thermolysis of *tert*-butylphosphaacetylene (**1**) gives rise to five different tetrameric cage skeletons. Furthermore, cyclotetramers are accessible more selectively by transition-metal-mediated, Lewis acid- and base-induced routes, as well as by starting with preformed phosphaalkyne cyclotrimers. It should be noted that, in the absence of a metal or Lewis acid, cyclotetramerization is indeed the preferred cyclooligomerization route for kinetically stabilized phosphaalkynes. In the coordination sphere of a metal, cyclodi- and -trimerizations are the predominant processes. However, after liberation of the organophosphorus ligand and subsequent reactions, the cyclotetramers are again obtained in most cases. Cyclotetramers often exhibit unexpected structural and spectroscopic features (especially the tetraphosphacubane **5**), which are of great interest from a theoretical viewpoint. Most of the phosphaalkyne cyclotetramers selectively undergo valence isomerization reactions, even when complete reorganization of the cage skeleton occurs. Moreover, high-level ab initio MO calculations can satisfactorily account for the results of these rearrangements. Additionally, these studies predict the stability of several as yet unknown phosphaalkyne tetramers, again demonstrating that this chemistry is still an expanding field of research. Future investigations of the synthesis and reactivity, as well as of mechanistic aspects of the formation of these compounds, may lead to further surprising results.

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