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Imidovanadium(v) Complexes as Reaction Partners for Kinetically Stabilized Phosphaalkynes: Synthesis of 1,2,4-Azaphosphavanada(v)-cyclobutenes, 1,3,5-Triphosphabenzenes, and 1*H*-1,2,4-Azadiphospholes

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Dedicated to Professor A. Schmidpeter on the occasion of his 70th birthday

Abstract: Cycloaddition reactions of the kinetically stabilized phosphaalkynes **1** with the imidovanadium(v) trihalides **9** furnish the 1,2,4-azaphosphavanada(v)cyclobutenes **10**. The stability of these novel metallacyclic compounds depends solely on the substitutents of the imido unit. Thus, the imidovanadium(v) species **9** with tertiary alkyl groups on the N atom form stable addition products with **1** while in the cases of compounds **9** with a lower degree of substitution at N (primary and secondary alkyl groups) the primarily formed adducts **10** undergo irreversible decomposition to afford the 1*H*-1,2,4-azadiphospholes **13**. Reactions of an excess of the phosphaaalkyne **1** with the vanadium complexes **9** furnish the corresponding triphosphabenzenes **8** in good yields (36–68%). A catalytic reaction course has been demonstrated for the all-*tert*-butyl system **1a/9a** in which the metallacyclic species **10a** serves as the catalytically active species. Poisoning of the catalyst leads to a second reaction pathway, which results in formation of the azatetraphosphaquadricyclanes **16**. By means of the stepwise use of different phosphaalkynes **1a**,**b** this methodology provides the first access to the differently substituted triphosphabenzenes through cyclotrimerization.

Keywords: cycloadditions · cyclooligomerizations · imidovanadium(v) complexes · phosphaalkynes · phosphorus heterocycles

Introduction

Cyclooligomerization reactions of phosphaalkynes, especially those of the kinetically stabilized type **1**, are important processes in the current research on low-coordinated phosphorus compounds.[1, 2, 3] Purely thermal reactions are always unspecific and generally lead to tetramerization products.[4] Specific cyclooligomerization reactions have only been realized in the presence of organometallic auxiliary compounds and proceed with incorporation of the metal complex fragment.

Thus, dimers, trimers, and tetramers of the phosphaalkynes have been constructed in the coordination spheres of transition metals.[5, 6, 7] In general, phosphaalkynes preferentially undergo cyclization to afford 1,3-diphosphacyclobutadienes in the presence of electron-rich transition metal fragments, while in the presence of the in situ generated 14 valence electron species Cp_2Zr they react to furnish the tricyclic complexes **3**.[5a,b] The cyclotrimerization of *tert*-butylphosphaalkyne **1a** on unsaturated [(Cot)Hf] transition metal templates represented a major breakthrough in this research. The reaction of (η^4-butadiene)Hf(Cot) **6** with **1a** at low temperature furnished the complex **7** (Scheme 1).[6a] When the same reaction was performed at 25 °C it proceeded through smooth tetramerization of **1a** with formation of hafnium-tetraphosphabarrelene complex.[7] A common feature of all currently known, transition metal induced cyclooligomerization reactions of phosphaalkynes, however, is the incorporation of the metal complex fragment in the reaction product. The first successful liberation of a metal-bound phosphaalkyne oligomer was realized with an early transition metal complex through oxidation of the metal fragment by hexachloroethane; both stable and unstable cyclooligomers were released in this way.

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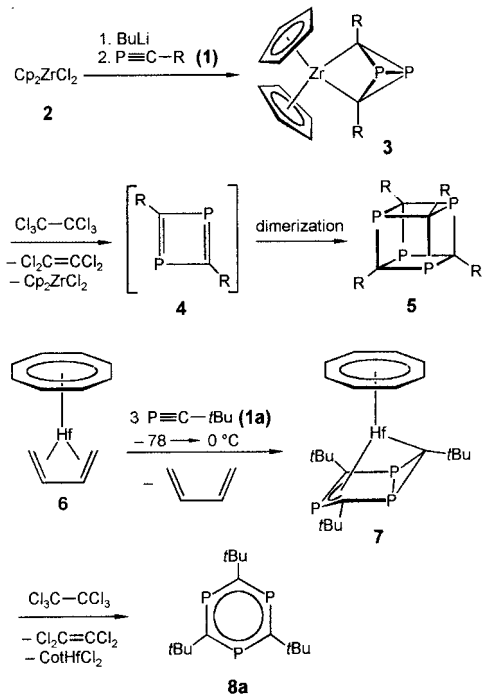
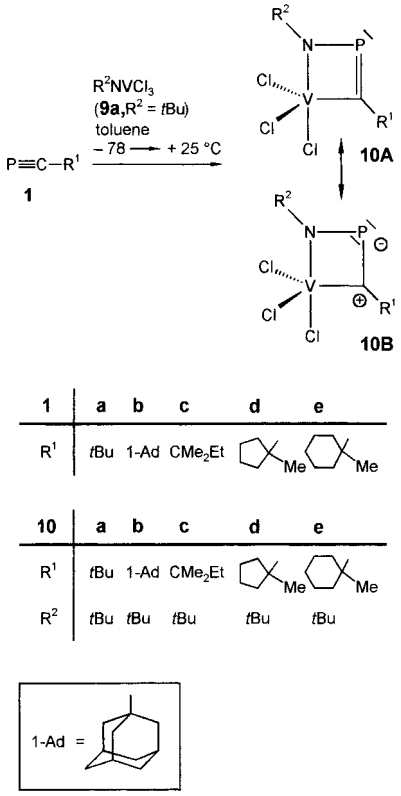


Scheme 1. Cyclooligomerization of phosphaalkynes **1**.



Scheme 2. Synthesis of complexes **10**.

This mild oxidation agent also effected the elimination of the zirconium fragment from **3** to liberate the highly reactive 1,3-diphosphacyclobutadiene **4**, which after further cyclodimerization could be isolated in high yield as the well known tetraphosphacuban.[8] The triphosphabenzene **8a**, which cannot be obtained by thermally induced cyclotrimerization, was first prepared by a comparable cleavage reaction from the η^8-cyclooctatetraene complex **7**. This synthetic strategy was also applied with success to prepare the Dewar-triphosphabenzene valence isomer of **8a** and the corresponding tetraphosphabarrelene.[6b]

We recently described the first cyclotrimerization of phosphaalkynes in the coordination sphere of *tert*-butylimidovanadium(v) trichloride **9a** which furnished the free 1,3,5-triphosphabenzenes **8** directly.[9] In this context we now report on the reactions between kinetically stabilized phosphaalkynes **1** and imidovanadium(v) complexes of the type **9**.

Results and Discussion

1,2,4-Azaphosphavanada(v)cyclobutene: Reactions of equimolar amounts of a phosphaalkyne **1a–e** with imidovanadium(v) trichloride **9a** proceed through [2+2] cycloaddition of the P≡C triple bond to the metal-nitrogen multiple bond to furnish the 1,2,4-azaphosphavanada(v)cyclobutenes **10a–e** which are stable at room temperature (Scheme 2). Performance of the reactions at low temperatures and exact observation of the stoichiometry are essential for the successful preparation of the metallacylic products **10**.

The formation of these novel complexes **10** from one equivalent each of phosphaalkyne **1** and vanadium halide **9a** is confirmed by their analytical and mass spectral data. The constitutions of the cycloaddition products are unambiguously apparent from their spectroscopic data. The NMR spectra of compounds **10** contain several structurally specific features (Figure 1) which are discussed below for the example of product **10a**. The ^{51}V NMR spectrum provides the first indication for the formation of the four-membered ring system: The chemical shift of $\delta = 310$ for **10a** is in the range

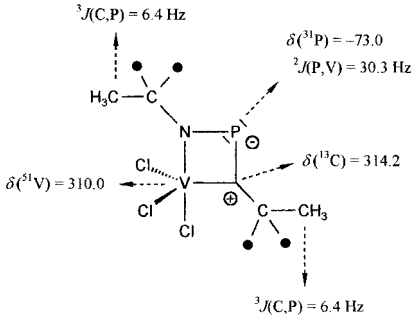


Figure 1. Characteristic NMR data of the metallacycle **10a**.

typical for a vanadium(v) compound with a metal–carbon bond.[10] The ^{1}H NMR spectrum of **10a** shows the two signals at $\delta = 1.39$ and 1.41 expected for the two *tert*-butyl groups (intensity ratio 1:1) with the signal at higher field being split into a doublet with a ^4J(H,P) coupling constant of 1.2 Hz. At highest field the ^{13}C{^{1}H} NMR spectrum reveals doublets at $\delta = 31.8$ and 32.9 with ^3J(C,P) coupling constants of 6.4 Hz for the methyl carbon atoms of the two *tert*-butyl groups. On account of the identical coupling constants it can safely be assumed that the phosphorus atom lies between the C and N atoms bearing the *tert*-butyl groups. The signal for the ring

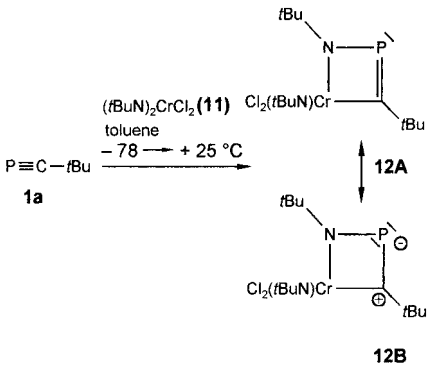
carbon atom is strongly shifted to low field ($\delta = 310.2$) and can only be observed at a high accumulation rate or at lower temperature (170 K); it is very broad and has a plateau-like appearance. Splittings attributable to the directly adjacent P and V atoms cannot be detected. Both the shape of the signal and the conditions required for its detection are typical phenomena always observed for vanadium-carbon compounds are due to quadrupole relaxations of the coupling ^{51}V nucleus (I = 7/2). The relaxation of the vanadium nucleus is only accelerated to such an extent by reducing the temperature that the resonances of the carbon atom become visible. This effect must also be held responsible for the absence of splitting and widening of the signals of the quaternary carbon atoms ($\delta = 55.9$ and 73.8) of the two *tert*-butyl groups. In the case of the *tert*-butyl group at the nitrogen atom the quadrupole effects of the ^{51}V and ^{14}N nuclei are complementary. The ^{31}P NMR spectrum of **10a** contains a signal at $\delta = -73.0$ for the ring phosphorus atom. This relatively strong shielding and the resultant high field shift has previously only been observed for phosphaalkynes with inverse electron densities.[11, 12] The deshielding of the neighboring ring carbon atom must also be viewed in this context and considered as being characteristic for systems of this type as well as emphasizing the electron situation (**10B**).

In analogy to ^{13}C NMR spectroscopy the quadrupole effect of the ^{51}V nucleus is also apparent from the characteristic signal shape and slight broadening of the signal.[10] However, this is markedly less pronounced than in complexes in which the vanadium atom is directly adjacent to the phosphorus atom.[13] The ^{2}J(P,V) coupling constant was determined by spectral simulation.[14] With a magnitude of 30.3 Hz it is markedly less than the range of known ^{1}J(P,V) coupling constants (160 – 480 Hz) and may thus be assigned to the previously unknown ^{2}J(P,V) coupling.[15, 16] Molecular weight measurement and analysis of the ^{51}V, ^{13}C, and ^{31}P NMR spectra unequivocally confirms that compounds **10** contain the previously unknown azaphosphametallacyclobutene ring system.

We have also examined the question of whether this cyclization reaction can be applied to the easily accessible bis(*tert*-butylimido)chromium(VI)dichloride **11**, in particular for the purpose of eliminating the disturbing quadrupole effect of the vanadium atom (pronounced line broadening), thus obtaining additional spectroscopic data in support of the four-membered ring structure. Indeed, reaction of the phosphaalkyne **1a** with an equimolar amount of **11** resulted in the quantitative formation of the metallacyclic product **12**.

In contrast to the reactions with the imidovanadium(V) complexes **9** neither the reaction temperature nor the stoichiometry has a significant effect on the course of the reaction. The possible second addition to the remaining metal-nitrogen multiple bond in **12** was not observed even in the presence of a large excess of the starting phosphaalkyne **1a**.

The ^{31}P NMR spectrum of **12** contains a singlet at $\delta = -76.2$. This chemical shift is almost identical with those seen for the vanadium-containing cycloaddition products **10** and can thus be considered to be typical for these four-membered ring systems with an inverse electron density of the phosphaalkene unit (**12A** ↔ **12B**) (Scheme 3).



Scheme 3. Synthesis of complex **12**.

The signals in the ^{13}C{^{1}H} NMR spectrum of **12** are of particular interest. As expected the ring carbon atom gives rise to a doublet signal at very low field ($\delta = 301.3$) with a ^{1}J(C,P) coupling constant of 108.6 Hz. Analogously, the quaternary carbon atoms of the two *tert*-butyl groups also couple with the ring phosphorus atom. The signal at $\delta = 65.9$ is assigned to the quaternary carbon atom of the *tert*-butyl group on nitrogen on account of its stronger shift to lower field and smaller ^{2}J(C,P) coupling while the doublet at $\delta = 49.9$ is assigned to that of the *tert*-butyl group on the carbon atom. The methyl carbon atoms give rise to signals at almost identical chemical shifts of $\delta = 34.1$ and 33.1 with comparable ^{3}J(C,P) coupling constants (8.6 and 7.3 Hz). The exocyclic *tert*-butylimido ligand gives rise to singlet signals at $\delta = 81.1$ and 31.4. The good agreement of the ^{31}P and ^{13}C NMR data for **10a** and **12** as well as the characteristic coupling constants of **12** support the proposed four-membered ring structure.

Changes in the alkyl group R^1 of the phosphaalkyne have no effect on the stability of the complexes **10** whereas changes in the alkyl group R^2 of the imido units of **9** do have a pronounced effect: Reactions of the trichlorides **9a–d** with **1a** furnish the stable and isolable [2 + 2] cycloaddition products **10a**, **f**, **g**, and **h** (Scheme 4), the metallacyclic species **10i–l** with secondary or primary alkyl groups on the ring nitrogen atom are merely detected as intermediates in the reaction mixture by spectroscopy (Table 1).

These unstable metallacyclic species **10i–l** undergo quantitative conversion to the 1*H*-1,2,4-azadiphospholes[17] **13a–d** within 24 h (Table 2).

NMR spectroscopic monitoring of the reaction does not provide information about possible intermediates which lead to products **13**. It can only be shown that after completion of the reaction the free imidovanadium component **9** is no longer present in the reaction mixture. Thus, although a simple transfer reaction of a phosphaalkyne unit between two molecules of the metallacyclic species **10** with liberation of one equivalent of **9** and subsequent reductive elimination of VCl_3 can be excluded, the mechanism of formation of **13** remains unknown.

Elemental analyses and mass spectral data clearly confirm that the heterodiphospholes are made up from two equivalents of phosphaalkyne **1a** with incorporation of the imido ligands from the vanadium compounds **9e–h**.

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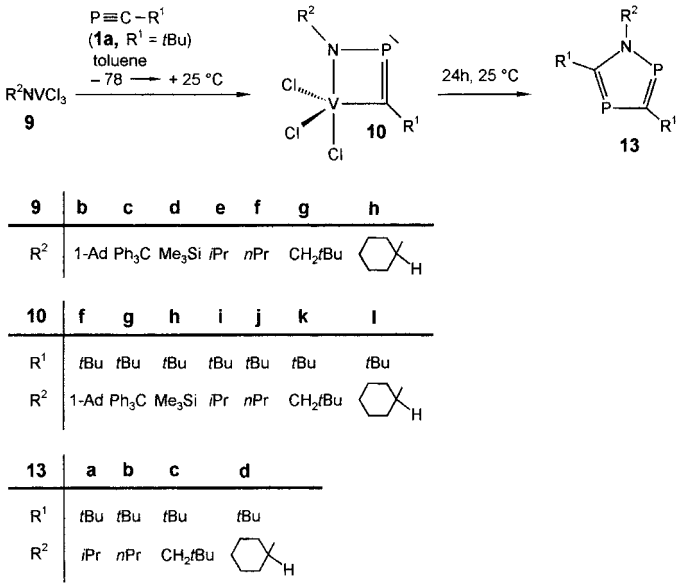


Scheme 4. Stable and unstable complexes **10**, synthesis of 1*H*-1,2,4-azadiphospholes **13**.

Table 1. Characteristic ^{51}V and ^{31}P NMR data of metallacycles **10** and **15**.

Compound	^{51}V NMR signal[a]	^{31}P NMR signal[a]
10a	310.0	– 73.0
10b	320.5	– 72.5
10c	312.3	– 71.9
10d	320.4	– 71.4
10e	317.2	– 71.8
10f	316.0	– 73.5
10g	380.3	– 64.8
10h	363.3	– 69.1
10i[b]	315.5	– 69.4
10j[b]	324.5	– 66.3
10k[b]	344.8	– 62.2
10l[b]	320.4	– 68.8
15	472.1	– 62.4

[a] Singlet. [b] Unstable intermediate.

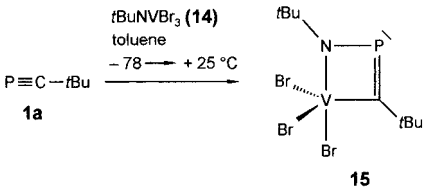
Table 2. Characteristic ^{31}P NMR data of 1*H*-1,2,4-azadiphospholes **13**.

Compound	^{31}P NMR[a]	^{2}J(P,P)
13a	148.1, 247.3	34.9
13b	154.1, 259.3	29.7
13c	148.6, 258.8	26.2
13d	127.1, 250.0	27.1

[a] Doublet.

The constitutions were elucidated on the basis of NMR spectroscopic studies as described below for the example of compound **13a**. The ^{1}H NMR spectrum with two signals each for the *tert*-butyl groups ($\delta = 1.63$ and 1.39) and the isopropyl groups ($\delta = 4.69$ and 1.38) demonstrates the unsymmetrical nature of the 1*H*-azadiphospholes although the splitting patterns of the couplings with the ring phosphorus atoms do not allow any firm conclusions on the arrangement of the two P atoms in the ring (2,4 or 2,3 positions). The ^{31}P NMR spectrum exhibits a characteristic AX spin system for the two phosphorus atoms in the low field region typical for heterodiphospholes ($\delta = 247.3$ and 148.1).[18] This splitting pattern and the resultant coupling constant of 34.9 Hz is only compatible with a 2,4-arrangement of the two P atoms. The ^{13}C NMR data for the ring carbon atoms C-3 and C-5 unequivocally confirm the constitution. Because of its coupling with the two directly adjacent atoms P-2 and P-4 the signal for the carbon atom C-3 ($\delta = 202.2$) is split into a double doublet with two almost identical ^{1}J(C,P) coupling constants of 62.3 and 52.5 Hz. A double doublet signal is also observed for C-5 ($\delta = 193.8$) but with a small coupling to P-2 [^{2}J(C,P) = 3.7 Hz] and a ^{1}J(C,P) coupling of 59.8 Hz to P-4.

Although changes in the alkyl rest bonded to the imido nitrogen atom had clear effects on the stability of the cycloaddition products **10**, exchange of the halogen atoms (Cl → Br) did not result in any changes in this reaction. Thus, cyclization of **1a** with **14** also proceeded smoothly to furnish the stable bromo analogue **15** (Scheme 5).



Scheme 5. Synthesis of complex **15**.

As expected, the formal exchange of three chlorine atoms for three bromine atoms at the metal center resulted in a low field shift of the ^{51}V NMR signal of **15** ($\delta = 472$) with all other NMR data remaining in harmony with those of the chlorine derivative **10a**; thus no detailed discussion is necessary.

1,3,5-Triphosphabenzenes: On reaction with an excess of the cycloaddition partners **1a–e** (4 equiv) under otherwise comparable conditions, compound **9a** afforded the substituted triphosphabenzenes **8a–e**, which were obtained as yellow solids after column chromatographic work-up with the exception of **8c** (yellow oil).

The easy accessibility of the cyclotrimerization starting product **9a**, the generally satisfactory yields (36–68%), and the one-pot procedure represent major advantages over the previously reported syntheses of **8a** and **8b**,[6b,c] the only previously known examples of the 1,3,5-triphosphabenzenes; thus the reaction opens a novel and simple approach to this class of compounds.

Elemental analyses and mass spectral data demonstrate the composition of compounds **8** from three phosphaalkyne building blocks. The constitutions of the new triphosphabenzenes **8c–e** is unequivocally supported by their spectroscopic data and comparison with the previously known compounds **8a**,**b** (Table 3).[6b,c]

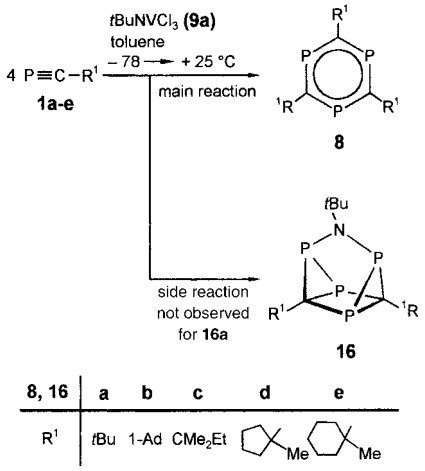
Table 3. Characteristic ^{31}P and ^{13}C NMR data of triphosphabenzenes **8**.

Compound	**8a**	**8b**	**8c**	**8d**	**8e**
^{31}P NMR[a]	232.6	238.1	238.8	234.2	242.8
^{13}C NMR[b]	211.8	212.2	208.8	211.8	212.1

[a] Singlet. [b] X part of A_2BX spin system.

As to be expected from the C_3 symmetry of the molecules, the ^{31}P NMR spectra each show a singlet signal in the region characteristic for phosphinines ($\delta = 234.2 - 242.8$).[19] Besides the less important signals for the individual substituents (see Experimental Section), the ^{13}C NMR spectra of **8c–e** contain the structurally relevant signals for the ring carbon atoms between $\delta = 208.8 - 212.2$. Their coupling patterns correspond to the X part of an A_2BX spin system.

In the case of the reaction of **9a** with **1a** the process is product specific for **8a** (**16a** cannot be detected), whereas on the other hand low levels of formation of the azatetraphosphaquadricylanes **16b–e** can be observed in the cyclotrimerizations of the phosphaalkynes **1b–e** (Scheme 6). The



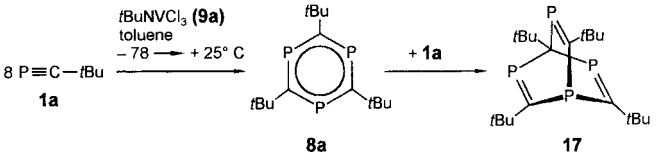
Scheme 6. Synthesis of 1,3,5-triphosphabenzenes **8**.

heterocyclic compounds **16** can also be obtained selectively by the reaction between the DME adduct of **9a** with the corresponding phosphaalkyne.[9, 20] The trimethylsilylimidovanadium(v) trichloride **9d** or tribromide **14** may also be used for the preparation of **8a**; these species exhibit an identical reaction behavior to **9a** in the presence of an excess of the phosphaalkyne **1a** (4 equiv), but are not synthetically advantageous on account of their more difficult syntheses.

The participation of the metallacylic species **10** in the cyclotrimerization process is clearly apparent: Compound **10** can always be detected by spectroscopy at the end of the reaction and is thus involved in the cyclotrimerization. When **10a** is allowed to react with two or three equivalents of **1a** the formation of the triphosphabenzene **8a** in the expected yield is observed. Other intermediates to **8a** cannot be identified. The reaction of **9a** with two or three equivalents of **1a** also furnishes the cyclotrimerization product **8a** directly. In all reactions of **9a** with more than one equivalent of **1a** it is clear that one equivalent of the cycloaddition partner is always required for the formation of the metallacyclic species **10a** which is also present in the solution after completion of the trimerization reaction.

Consideration of these facts allows only one conclusion, namely that the formation of the 1,3,5-triphosphabenzenes **8** is a catalytic process and that the metallacyclic compound **10** is the catalytically active species. In order to confirm this hypothesis, compound **9a** was allowed to react with eight equivalents of *tert*-butylphosphaalkyne **1a**.

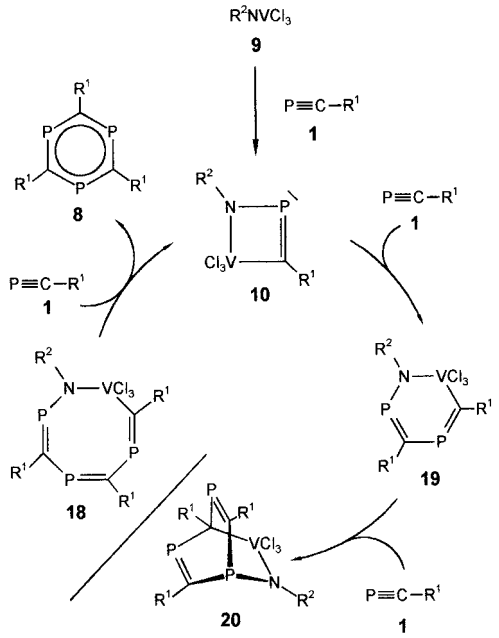
Column chromatographic work-up analogous to that used for the 1:4 reaction furnished **8a** in a comparable yield of 68% referred to the employed phosphaalkyne. The magnitude of this yield unambiguously supports the catalytic nature of the reaction. The renewed formation of the catalyst, as a typical feature of catalytic reactions, is confirmed by $^{31}P/^{51}V$ NMR spectroscopy. Besides **10a**, ^{31}P NMR spectroscopic monitoring of the reaction solution reveals the presence of traces of the tetraphosphabarrelene **17**[6] (Scheme 7) and the azatetraphos-



Scheme 7. Catalytic cyclotrimerization of **1a**.

phaquadricyclane **16a**.[9, 20] Although the formation of the barrelene **17** can be considered as a known subsequent reaction of **1a** with **8a**,[21] the formation of the azatetraphosphaquadricyclane is most certainly an alternative reaction pathway proceeding with destruction of the catalyst.

The proposed reaction mechanism for the cyclotrimerization process is as follows (Scheme 8): The first step involves a



Scheme 8. Proposed reaction mechanism for the cyclotrimerization of **1**.

[2 + 2]-cycloaddition reaction between **9** and **1** with formation of the metallacyclic species **10**. Insertion of a further molecule of **1** into the metal–carbon bond affords the intermediate **19**. This six-membered ring species can undergo both ring expansion with a third equivalent of **1** to give the metallacyclooctatriene **18** and a [4 + 2] Diels–Alder reaction to form the metallabarrelene derivative **20**. The reaction step with a fourth equivalent of **1** completing the cycle results in

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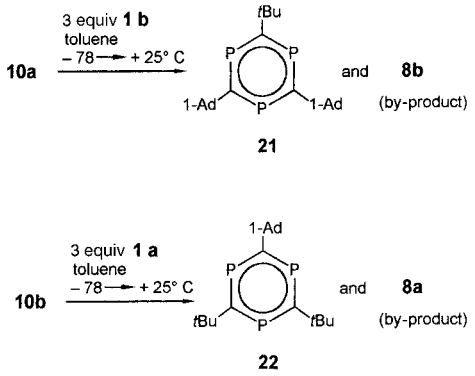
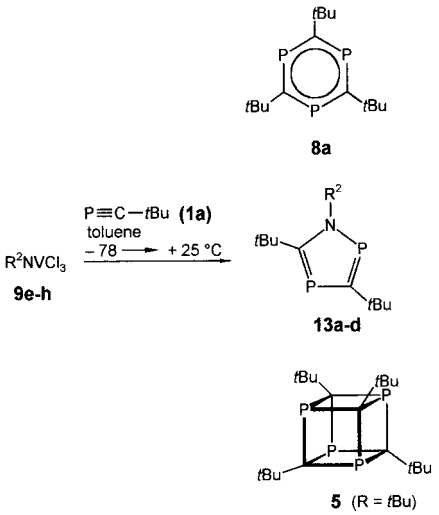
liberation of the 1,3,5-triphosphabenzene **8** with renewed formation of the catalyst **10**. The catalytic sequence is interrupted when the insertion of a molecule of **1** does not occur in the metal–carbon but rather in the metal–nitrogen bond of **10**. As already reported, this leads to formation of the azatetraphosphaquadricyclane **16** with irreversible destruction of the catalyst.[9, 20] Further support of the catalytic trimerization process is provided by the reactions of the metallacyclic species **10a**,**b** with the phophaalkynes **1b**,**a**. Besides the known uniformly substituted heteroaromatic products **8** these reactions represent the first accesses to the differently substituted derivatives **21** and **22**. The different products obtained conclusively confirms that **10a**, **10b** participate both in the formation of the unsymmetrically substituted triphosphabenzenes **21**, **22** as well as, after their renewed formation as **10b**, **10a** in the catalytic process. The symmetrically substituted 1,3,5-triphosphabenzenes **8a**,**b** are then formed in a further reaction sequence (Scheme 9).



Scheme 9. Synthesis of 1,3,5-triphosphabenzenes **21** and **22**.

The separation of the two compounds was not possible, even by column chromatography. However, the identities of the novel heteroaromatic compounds **21** and **22** were unequivocally demonstrated by analysis of the ^{31}P NMR spectrum of the reaction mixture and by mass spectroscopy. In both cases the molecular ion peaks for **21**, **22**, respectively, were observed together with those for the known 1,3,5-triphosphabenzenes **8a**,**b**. The ^{31}P NMR spectrum of the mixture **21**, **22** contains signals with the characteristic AB_2 spin systems for the substitution pattern with ^2J(P,P) coupling constants of 6.2 and 7.9 Hz. With ^{31}P NMR chemical shifts of $\delta = 235.4/235.2$ and 237.2/237.0, respectively, compounds **21**, **22** fit into the series between the uniform *tert*-butyl and the uniform 1-adamantyl derivatives **8a**,**b**. The close relationship of products **21**, **22** with the corresponding symmetrical derivatives **8b**,**a** is also documented by their chemical shifts; thus, for example, the signals of **22** are markedly closer to those of **8a** than to those of **8b** on account of its higher content of *tert*-butyl groups.

As expected in analogy to the 1:1 reactions, variation of the alkyl group on the imido ligand in **9** does result in a change in the reaction behavior. Although the trimethylsilyl derivative **9d** also reacts with an excess of **1a** (4 equiv) to furnish the trimer **8a** exclusively; reaction of the 1-adamantyl derivative **9b** under comparable conditions affords the *N*-adamantyl-substituted azatetraphosphaquadricyclane as a by-product.[20] Subsequent reactions of the triphenylmethyl-substituted metallacyclic species **10g** with **1a** were completely suppressed. Among the trimerization reagents **9** the imido trichlorides **9e–h** bearing secondary or primary alkyl groups again occupy a special position. Although their reactions with four equivalents of *tert*-butylphosphaalkyne **1a** also resulted in the formation of the 1,3,5-triphosphabenzene **8a**, the tetraphosphacubane **5**[8] and the corresponding 1*H*-azadiphosphole **13** were also formed in comparable amounts (Scheme 10).



Scheme 10. Reaction of complexes **9e–h** bearing secondary or primary alkyl groups with four equivalents **1a**.

While the formation of **13** had already been observed as a result of decomposition reactions during the preparation of the unstable metallacyclic compounds **10i–l**, the formation of the tetraphosphacubane **5** is rather a surprising result in this case. ^{31}P NMR spectroscopic monitoring of the reaction clearly reveals the primary formation of the triphosphabenzene **8a**. This process, however, comes to a halt with increasing reaction time with a parallel increase in the formation of the 1*H*-azadiphosphole **13**. The increasing concentration of the 1*H*-azadiphosphole is accompanied by a pronounced formation of the cubane **5** (Scheme 10) which finally becomes the dominating reaction. In the final stages only an increase in the concentration of the cubane can be observed while the contents of **8a** and **13** in the solution remain constant.

The ready availability of the 1,3,5-triphosphabenzenes **8** and the 1*H*-1,2,4-azadiphospholes **13** have enabled us to study the reactivity of these two phosphorus-containing heterocyclic systems. In accord with our current research interests emphasis will be placed on the addition and cycloaddition behavior of these species.

Experimental Section

General: All experiments were carried out under argon (purity > 99.998 %) in previously evacuated and oven-dried Schlenk vessels. The solvents are anhydrous and stored under argon prior to use. NMR spectra were

recorded on Bruker WP 200 and AM 400 instruments. Chemical shifts for the ^{1}H and ^{13}C NMR nuclei are reported in parts per million (δ) relative to tetramethylsilane as the internal standard; chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid and ^{51}V are relative to external $VOCl_3$. Elemental analyses were performed on Perkin–Elmer Analyser EA 240 and 2400 CHN. Bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus (temperatures given refer to the heating mantle). Mass spectra were recorded on a Finnigan MAT 90 spectrometer. Starting compounds **1a**,[22a,b] **1b**,[22c] **1c**,[22d] **1d**,**e**,[22e] **9a**,[23a,b] **9b–h**,[23d] **11**,[24] and **14**[23c] were prepared by published methods.

General procedure for the preparation of the metallacycles 10a–h, 12, and 15: An equimolar amount of phosphaalkyne **1** was added at −78 °C to a solution of the imido compound **9**, **11**, or **14** in toluene. The mixture was allowed to warm up and the solvent was removed at 20 °C at 10^{-2} mbar. The metallacyclic products were obtained as dark residues in quantitative yield.

1,3-Di-*tert*-butyl-4,4,4-trichloro-1-aza-2-phospha-4-vanada(v)cyclobut-2-ene (10a): Compound **9a** (260 mg, 1.15 mmol) in toluene (5 mL) and **1a** (120 mg, 1.15 mmol) afforded **10a** (380 mg, 100%) as a brown powder. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 1.39 [s, 9H, C(C*H*)$_3$], 1.41 [d, ^4J(H,P) = 1.2 Hz, 9H, C(C*H*)$_3$]; ^{13}C NMR (C_6D_6, 50.3 Hz, 170 K): δ = 31.8 [d, ^3J(C,P) = 6.4 Hz, C(CH_3)$_3$], 32.9 [d, ^3J(C,P) = 6.4 Hz, C(*C*H$_3$)$_3$], 55.9 [s, C*C*(CH$_3$)$_3$], 73.8 [s, N*C*(CH$_3$)$_3$], 314.2 [s, *CC*(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −73.0 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 310.0 [s, $\nu_{1/2}$ = 209 Hz]; MS (70 eV, EI): *m*/*z* (%): 327 (2) $[M]^+$, 270 (7) $[M - C_4H_9]^+$, 235 (6) $[M - C_4H_9Cl]^+$, 57 (100) $[C_4H_9]^+$; molecular weight (cryosc, C_6H_6): calcd 328.52, found 345; elemental analysis calcd for $C_9H_{18}Cl_3NPV$ (328.52): C 32.90, H 5.52, N 4.26; found C 32.7, H 5.5, N 4.1.

3-(1-Adamantyl)-1-*tert*-butyl-4,4,4-trichloro-1-aza-2-phospha-4-vanada(v)cyclobut-2-ene (10b): Compound **9a** (130 mg, 0.41 mmol) in toluene (5 mL) and **1b** (40 mg, 0.41 mmol) furnished **10b** (170 mg, 100%) as a brown powder. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 1.50–2.40 [m, 15H, Ad-*H*], 1.61 [s, 9H, C(C*H*)$_3$]; ^{13}C NMR (C_6D_6, 50.3 Hz, 25 °C): δ = 29.2 [d, ^4J(C,P) = 1.1 Hz, Ad-*C*H], 32.8 [d, ^3J(C,P) = 5.5 Hz, NC(*C*H$_3$)$_3$], 36.0 [s, Ad-*C*H$_2$], 44.4 [d, ^3J(C,P) = 7.6 Hz, Ad-*C*H$_2$], 60.0 [m, Ad-*C*], 73.5 [m, N*C*(CH$_3$)$_3$], [ring-*C*)] not found; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −72.5 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 320.5 [s, $\nu_{1/2}$ = 193 Hz]; MS (70 eV, EI): *m*/*z* (%): 405 (7) $[M]^+$, 178 (76) $[PC(1-Ad)]^+$, 57 (100) $[C_4H_9]^+$; $C_{15}H_{24}Cl_3NPV$ (406.63).

1-*tert*-Butyl-4,4,4-trichloro-3-(1,1-dimethylpropyl)-1,2,4-azaphosphavanada(v)cyclobut-2-ene (10c): Compound **9a** (228 mg, 1.00 mmol) in toluene (5 mL) and **1c** (114 mg, 1.00 mmol) furnished **10c** (342 mg, 100%) as a black-brown oil. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 0.96 [t, ^3J(H,H) = 7.1 Hz, 3H, CH$_2$C*H*$_3$], 1.33 [s, 6H, C(C*H*$_3$)$_2$C$_2$H$_5$], 1.43 [s, 9H, NC(C*H*$_3$)$_3$], 1.81 [q, ^3J(H,H) = 7.1 Hz, 2H, C*H*$_2$CH$_3$] ; ^{13}C NMR (C_6D_6, 50.3 Hz, 25 °C): δ = 10.5 [d, ^4J(C,P) = 1.2 Hz, CH$_2$*C*H$_3$], 29.7 [d, ^3J(C,P) = 7.0 Hz, C(*C*H$_3$)(CH$_3$)C$_2$H$_5$], 29.9 [d, ^3J(C,P) = 8.2 Hz, C(CH$_3$)(*C*H$_3$)C$_2$H$_5$], 33.5 [d, ^3J(C,P) = 4.7 Hz, NC(*C*H$_3$)$_3$], 38.5 [d, ^3J(C,P) = 4.7 Hz, *C*H$_2$CH$_3$], 60.6 [m, *C*C(CH$_3$)$_2$C$_2$H$_5$], 74.2 [m, N*C*(CH$_3$)$_3$], 317.7 [m, *C*C(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −71.9 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 312.3 [s, $\nu_{1/2}$ = 205 Hz]; MS (70 eV, EI): *m*/*z* (%): 341 (1) $[M]^+$, 306 (1) $[M - Cl]^+$, 285 (4) $[M - C_4H_8]^+$, 57 (100) $[C_4H_9]^+$; $C_{10}H_{20}Cl_3NPV$ (342.44).

1-*tert*-Butyl-4,4,4-trichloro-3-(1-methylcyclopentyl)-1,2,4-azaphosphavanada(v)cyclobut-2-ene (10 d): Compound **9a** (228 mg, 1.00 mmol) in toluene (5 mL) and **1d** (126 mg, 1.00 mmol) furnished **10d** (354 mg, 100%) as a black-brown oil. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 0.85–2.05 [m, 8H, cyclopentyl-C*H*$_2$], 1.32 [s, 3H, C*H*$_3$], 1.42 [s, 9H, NC(C*H*$_3$)$_3$]; ^{13}C NMR (C_6D_6, 50.3 Hz, 25 °C): δ = 24.7 [s, cyclopentyl-*C*H$_2$], 28.4 [d, ^3J(C,P) = 7.6 Hz, *C*H$_3$], 32.5 [s, NC(*C*H$_3$)$_3$], 42.7 [d, ^3J(C,P) = 4.2 Hz, cyclopentyl-*C*H$_2$], 43.6 [d, ^3J(C,P) = 7.6 Hz, cyclopentyl-*C*H$_2$], 67.6 [m, *C*C(CH$_2$)$_2$CH$_3$], 73.6 [m, N*C*(CH$_3$)$_3$], [*CC*(CH$_3$)$_3$] not found; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −71.4 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 320.4 [s, $\nu_{1/2}$ = 208 Hz]; MS (70 eV, EI): *m*/*z* (%): 353 (1) $[M]^+$, 297 (3) $[M - C_4H_8]^+$, 267 (100) $[M - C_6H_{14}]^+$, 126 (4) $[PC(C_5H_8)CH_3]^+$; $C_{11}H_{20}Cl_3NPV$ (354.55).

1-*tert*-Butyl-4,4,4-trichloro-3-(1-methylcyclohexyl)-1,2,4-azaphosphavanada(v)cyclobut-2-ene (10e): Compound **9a** (228 mg, 1.00 mmol) in toluene (5 mL) and **1e** (140 mg, 1.00 mmol) furnished **10e** (368 mg, 100%) as a black-brown oil. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 0.90–2.12 [m, 10H, cyclohexyl-C*H*$_2$], 1.22 [s, 3H, C*H*$_3$], 1.44 [s, 9H, NC(C*H*$_3$)$_3$]; ^{13}C NMR (C_6D_6, 50.3 Hz, 25 °C): δ = 23.7 [d, ^3J(C,P) = 5.9 Hz, *C*H$_3$], 25.9 [s, cyclohexyl-*C*H$_2$], 28.9 [d, ^4J(C,P) = 2.3 Hz, cyclohexyl-*C*H$_2$], 29.0 [d, ^4J(C,P) = 2.3 Hz, cyclohexyl-*C*H$_2$], 33.1 [d, ^3J(C,P) = 5.9 Hz, NC(*C*H$_3$)$_3$], 41.5 [d, ^3J(C,P) = 7.0 Hz, cyclohexyl-*C*H$_2$], 41.8 [d, ^3J(C,P) = 8.2 Hz, cyclohexyl-*C*H$_2$], 62.4 [m, C*C*(CH$_2$)$_2$CH$_3$], 73.9 [m, N*C*(CH$_3$)$_3$], [*CC*(CH$_3$)$_3$] not found; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −71.8 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 317.2 [s, $\nu_{1/2}$ = 214 Hz]; MS (70 eV, EI): *m*/*z* (%): 367 (7) $[M]^+$, 311 (36) $[M - C_4H_8]^+$, 275 (22) $[M - C_4H_9Cl]^+$, 57 (100) $[C_4H_9]^+$; $C_{12}H_{22}Cl_3NPV$ (368.59).

1-(1-Adamantyl)-3-*tert*-butyl-4,4,4-trichloro-1-aza-2-phospha-4-vanada(v)-cyclobut-2-ene (10f): Compound **9b** (130 mg, 0.41 mmol) in toluene (5 mL) and **1a** (40 mg, 0.41 mmol) furnished **10f** (170 mg, 100%) as a brown powder. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 1.41–2.20 [m, 15H, Ad-*H*], 1.52 [s, 9H, C(C*H*$_3$)$_3$]; ^{13}C NMR (C_6D_6, 50.3 Hz, 25 °C): δ = 30.8 [s, Ad-*C*H$_2$], 31.9 [d, ^3J(C,P) = 6.6 Hz, C(*C*H$_3$)$_3$], 35.7 [s, Ad-*C*H], 47.0 [d, ^3J(C,P) = 4.0 Hz, Ad-*C*H$_2$], 55.9 [s, *CC*(CH$_3$)$_3$], 75.9 [s, Ad-*C*], [*CC*(CH$_3$)$_3$] not found; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −73.5 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 316.0 [s, $\nu_{1/2}$ = 193 Hz]; MS (70 eV, EI): *m*/*z* (%): 135 (80) $[C_{10}H_{15}]^+$, 92 (100) $[C_7H_8]^+$, 57 (8) $[C_4H_9]^+$; $C_{15}H_{24}Cl_3NPV$ (406.63).

1-*tert*-Butyl-4,4,4-trichloro-3-(triphenylmethyl)-1,2,4-azaphosphavanada(v)cyclobut-2-ene (10g): Compound **9c** (271 mg, 0.65 mmol) in toluene (5 mL) and **1a** (65 mg, 0.65 mmol) furnished **10g** (336 mg, 100%) as a brown powder. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 1.43 [d, ^4J(H,P) = 7.3 Hz, 9H, C(C*H*)$_3$], 6.90–7.50 [m, 15H, Ph]; ^{13}C NMR (C_6D_6, 50.3 Hz, 25 °C): δ = 31.9 [d, ^3J(C,P) = 7.5 Hz, C(*C*H$_3$)$_3$], 55.9 [s, C*C*(CH$_3$)$_3$], 95.7 [s, *C*(C$_6$H$_5$)$_3$], 141.6 [s, C(*C*$_6$H$_5$)$_3$], 143.8 [s, C(*C*$_6$H$_5$)$_3$], 145.8 [s, C(*C*$_6$H$_5$)$_3$], 149.0 [s, C(*C*$_6$H$_5$)$_3$], 314.6 [s, *CC*(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −64.8 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 380.3 [s, $\nu_{1/2}$ = 230 Hz]; MS (70 eV, EI): *m*/*z* (%): 257 (3) $[NCPh_3]^+$, 243 (7) $[CPh_3]^+$, 77 (100) $[Ph]^+$; $C_{23}H_{24}Cl_3NPV$ (502.73): calcd C 56.00, H 4.70, N 2.72; found C 55.1, H 4.6, N 2.4.

1-*tert*-Butyl-4,4,4-trichloro-3-(trimethylsily)-1,2,4-azaphosphavanada(v)-cyclobut-2-ene (10h): Compound **9d** (177 mg, 0.73 mmol) in toluene (5 mL) and **1a** (73 mg, 0.73 mmol) furnishes **10h** (250 mg, 100%) as a black-brown oil. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 0.12 [s, 9H, SiMe$_3$], 1.45 [d, ^4J(H,P) = 0.8 Hz, 9H, C(C*H*)$_3$]; ^{13}C NMR (C_6D_6, 50.3 Hz, 170 K): δ = 2.1 [s, Si(*C*H$_3$)$_3$], 30.9 [d, ^3J(C,P) = 6.4 Hz, C(*C*H$_3$)$_3$], 55.9 [s, *C*C(CH$_3$)$_3$], 316.4 [s, *CC*(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −69.1 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 363.3 [s, $\nu_{1/2}$ = 240 Hz]; $C_8H_{18}Cl_3NPSiV$ (344.60).

1,3-Di-*tert*-butyl-4,4,-dichloro-4-tert-butylimido-1-aza-4-chroma(VI)-2-phosphacyclobut-2-ene (12): Compound **11** (180 mg, 0.66 mmol) in toluene (5 mL) and **1a** (70 mg, 0.70 mmol) furnished **12** (246 mg, 100%) as a green powder. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 1.24 [s, 9H, C(C*H*$_3$)$_3$], 1.32 [s, 9H, C(C*H*$_3$)$_3$], 1.44 [d, ^4J(H,P) = 1.1 Hz, 9H, C(C*H*$_3$)$_3$]; ^{13}C NMR (C_6D_6, 50.3 Hz, 170 K): δ = 31.4 [s, C(*C*H$_3$)$_3$], 33.1 [d, ^3J(C,P) = 7.3 Hz, C(*C*H$_3$)$_3$], 34.1 [d, ^3J(C,P) = 8.6 Hz, C(*C*H$_3$)$_3$], 49.9 [d, ^2J(C,P) = 19.5 Hz, *C*C(CH$_3$)$_3$], 65.9 [d, ^2J(C,P) = 12.2 Hz, N*C*(CH$_3$)$_3$], 81.1 [s, N*C*(CH$_3$)$_3$], 301.3 [d, ^1J(C,P) = 108.6 Hz, *C*C(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −76.2 (s); MS (70 eV, EI): *m*/*z* (%): 364 (16) $[M]^+$, 349 (17) $[M - CH_3]^+$, 293 (67) $[M - C_4H_9N]^+$, 57 (100) $[C_4H_9]^+$; $C_{13}H_{27}Cl_2CrN_2P$ (365.3).

4,4,4-Tribromo-1,3-di-*tert*-butyl-1-aza-2-phospha-4-vanada(v)cyclobut-2-ene (15): Compound **14** (160 mg, 0.45 mmol) in toluene (5 mL) and **1a** (45 mg, 0.45 mmol) furnished **15** (205 mg, 100%) as a red-brown powder. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 1.48 [s, 9H, C(C*H*$_3$)$_3$], 1.50 [s, 9H, C(C*H*$_3$)$_3$]; ^{13}C NMR (C_6D_6, 50.3 Hz, 25 °C): δ = 32.0 [d, ^3J(C,P) = 6.6 Hz, C(*C*H$_3$)$_3$], 33.0 [d, ^3J(C,P) = 6.6 Hz, C(*C*H$_3$)$_3$], 56.0 [s, *C*C(CH$_3$)$_3$], 74.3 [s, N*C*(CH$_3$)$_3$], 319.0 [s, *CC*(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz, 25 °C): δ = −62.4.0 (s); ^{51}V NMR (C_6D_6, 52.6 MHz, 25 °C): δ = 472.1 [s, $\nu_{1/2}$ = 191 Hz]; MS (70 eV, EI): *m*/*z* (%): 349 (2) $[M - C_8H_{16}]^+$, 100 (5) $[C_5H_9P]^+$, 57 (100) $[C_4H_9]^+$; $C_9H_{18}Br_3NPV$ (461.88).

General procedure for the preparation of the 1*H*-1,2,4-azadiphospholes 13a–d: An equimolar amount of phosphaalkyne **1a** at −78 °C was added to a solution of the imidovanadium compound **9e–h** in toluene. The mixture was allowed to warm up, stirred for 24 h at room temperature, and then the solvent was removed at 20 °C at 10^{-2} mbar. After extraction with *n*-pentane (20 mL), the solvent was distilled off under reduced pressure (20 °C at 10^{-2} mbar), and the residue purified by bulb-to-bulb distillation.

3,5-Di-*tert*-butyl-1-isopropyl-1,2,4-azadiphosphole (13a): Compound **9e** (140 mg, 0.63 mmol) and **1a** (63 mg, 0.63 mmol) furnished **13a** (55 mg, 67%) as a white powder (b.p. 130 °C at 10^{-2} mbar); ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ = 1.38 [d, ^3J(H,H) = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$], 1.39 [d,

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^4J(H,P) = 2.2 Hz, 9H, C(CH_3)$_3$], 1.63 [dd, ^4J(H,P) = 1.8, 0.7 Hz, 9H, C(CH_3)$_3$], 4.69 [dsept, ^3J(H,H) = 6.6 Hz, ^3J(H,P) = 2.7 Hz, 1H, CH(CH$_3$)$_2$]; ^{13}C NMR (C$_6$D$_6$, 50.3 Hz, 25 °C): δ = 27.6 [d, ^3J(C,P) = 12.1 Hz, CH(CH_3)$_2$], 32.0 [d, ^3J(C,P) = 13.4 Hz, C(CH_3)$_3$], 35.4 [dd, ^3J(C,P) = 11.0, 8.6 Hz, C(CH_3)$_3$], 37.4 [dd, ^2J(C,P) = 21.8, 17.3 Hz, C(CH$_3$)$_3$], 38.2 [dd, ^2J(C,P) = 19.1, ^3J(C,P) = 2.5 Hz, C(CH$_3$)$_3$], 53.2 [dd, ^2J(C,P) = 17.1 Hz, ^3J(C,P) = 2.5 Hz, CH(CH$_3$)$_2$], 193.8 [dd, ^1J(C,P) = 59.8 Hz, ^2J(C,P) = 3.7 Hz, CC(CH$_3$)$_3$], 202.2 [dd, ^1J(C,P) = 62.3, 52.5 Hz, CC(CH$_3$)$_3$]; ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 148.1, 247.3 [each d, ^2J(P,P) = 34.9 Hz]; MS (70 eV, EI): m/z (%): 257 (29) $[M]^+$, 242 (6) $[M-CH_3]^+$, 200 (12) $[M-C_3H_7N]^+$, 84 (100) $[C_4H_5P]^+$; elemental analysis calcd for $C_{13}H_{25}NP_2$ (257.30): C 60.69, H 9.76, N 5.44; found C 59.7, H 9.8, N 5.1.

3,5-Di-*tert*-butyl-1-*n*-propyl-1,2,4-azadiphosphole (13b): Compound **9f** (118 mg, 0.28 mmol) and **1a** (28 mg, 0.28 mmol) furnished **13b** (39 mg, 55%) as a colorless oil (b.p. 140 °C at 10^{-2} mbar); ^{1}H NMR (C$_6$D$_6$, 200 MHz, 25 °C): δ = 0.81 [t, ^3J(H,H) = 6.8 Hz, 3H, CH$_2$CH$_2$CH_3], 1.36 [d, ^4J(H,P) = 1.6 Hz, 9H, C(CH_3)$_3$], 1.46 [ps, ^3J(H,H) = 6.8 Hz, 2H, CH$_2$CH_2CH$_3$], 1.62 [d, ^4J(H,P) = 1.8 Hz, 9H, C(CH_3)$_3$], 4.10 [m, 2H, CH_2CH$_2$CH$_3$]; ^{13}C NMR (C$_6$D$_6$, 50.3 Hz, 25 °C): δ = 11.35 [s, CH$_2$CH$_2$CH$_3$], 19.39 [d, ^3J(C,P) = 2.78 Hz, CH$_2$CH$_2$CH$_3$], 33.7 [d, ^3J(C,P) = 15.8 Hz, C(CH_3)$_3$], 35.7 [dd, ^3J(C,P) = 12.1, 9.2 Hz, C(CH$_3$)$_3$], 37.6 [dd, ^2J(C,P) = 33.8, 21.6 Hz, C(CH$_3$)$_3$], 38.7 [dd, ^2J(C,P) = 21.4 Hz, ^3J(C,P) = 3.0 Hz, C(CH$_3$)$_3$], 53.1 [dd, ^2J(C,P) = 15.4 Hz, ^3J(C,P) = 3.0 Hz, CH_2CH$_2$CH$_3$], 198.6 [dd, ^1J(C,P) = 45.4 Hz, ^2J(C,P) = 7.3 Hz, CC(CH$_3$)$_3$], 203.8 [dd, ^1J(C,P) = 45.1, 38.7 Hz, CC(CH$_3$)$_3$]; ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 154.1, 259.3 [each d, ^2J(P,P) = 29.7 Hz]; MS (70 eV, EI): m/z (%): 257 (100) $[M]^+$, 242 (4) $[M-CH_3]^+$, 214 (5) $[M-C_3H_7]^+$; $C_{13}H_{25}NP_2$ (257.30).

3,5-Di-*tert*-butyl-1-(2,2-dimethyl)propyl-1,2,4-azadiphosphole (13c): Compound **9g** (157 mg, 0.65 mmol) and **1a** (65 mg, 0.65 mmol) furnished **13c** (80 mg, 87%) as a white powder (b.p. 150 °C at 10^{-2} mbar); ^{1}H NMR (C$_6$D$_6$, 200 MHz, 25 °C): δ = 0.96 [s, 9H, CH$_2$C(CH_3)$_3$], 1.45 [d, ^4J(H,P) = 1.7 Hz, 9H, C(CH_3)$_3$], 1.64 [d, ^4J(H,P) = 1.5 Hz, 9H, C(CH_3)$_3$], 4.13 [dd, ^3J(H,P) = 14.4, ^4J(H,P) = 0.7, 2H, CH_2C(CH$_3$)$_3$]; ^{13}C NMR (C$_6$D$_6$, 50.3 Hz, 25 °C): δ = 28.8 [s, CH$_2$C(CH_3)$_3$], 30.25 [d, ^3J(C,P) = 2.4 Hz, CH$_2$C(CH$_3$)$_3$], 33.1 [d, ^3J(C,P) = 14.9 Hz, C(CH_3)$_3$], 35.4 [dd, ^3J(C,P) = 11.7, 8.6 Hz, C(CH_3)$_3$], 37.1 [dd, ^2J(C,P) = 34.8, 21.1 Hz, C(CH$_3$)$_3$], 38.5 [dd, ^2J(C,P) = 19.6 Hz, ^3J(C,P) = 3.9 Hz, C(CH$_3$)$_3$], 61.9 [dd, ^2J(C,P) = 16.4 Hz, ^3J(C,P) = 3.1 Hz, CH_2C(CH$_3$)$_3$], 195.6 [dd, ^1J(C,P) = 55.6 Hz, ^2J(C,P) = 4.5 Hz, CC(CH$_3$)$_3$], 202.0 [dd, ^1J(C,P) = 56.3, 36.0 Hz, CC(CH$_3$)$_3$]; ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 148.6, 258.8 [each d, ^2J(P,P) = 26.2 Hz]; MS (70 eV, EI): m/z (%): 285 (100) $[M]^+$, 270 (20) $[M-CH_3]^+$, 228 (5) $[M-C_5H_{11}N]^+$; $C_{15}H_{29}NP_2$ (285.35).

3,5-Di-*tert*-butyl-1-cyclohexyl-1,2,4-azadiphosphole (13d): Compound **9h** (199 mg, 0.78 mmol) and **1a** (78 mg, 0.78 mmol) furnished **13d** (71 mg, 61%) as a colorless oil (b.p. 180 °C at 10^{-2} mbar); ^{1}H NMR (C$_6$D$_6$, 200 MHz, 25 °C): δ = 0.76–2.15 [m, 28H, C(CH_3), cyclohexyl-CH_2], 4.33 [s, 1H, NCH]; ^{13}C NMR (C$_6$D$_6$, 50.3 Hz, 25 °C): δ = 22.7 [s, CH_2], 23.55 [s, CH_2], 27.30 [d, ^3J(C,P) = 4.5 Hz, CH_2], 33.9 [d, ^3J(C,P) = 14.5 Hz, C(CH$_3$)$_3$], 35.0 [dd, ^3J(C,P) = 10.39, 7.5 Hz, C(CH_3)$_3$], 37.1 [dd, ^2J(C,P) = 30.1, 18.0 Hz, C(CH$_3$)$_3$], 38.7 [dd, ^2J(C,P) = 20.0 Hz, ^3J(C,P) = 4.0 Hz, C(CH$_3$)$_3$], 56.9 [dd, ^2J(C,P) = 20.54, ^3J(C,P) = 5.4 Hz, NCH], 197.6 [dd, ^1J(C,P) = 50.0 Hz, ^2J(C,P) = 5.2 Hz, CC(CH$_3$)$_3$], 202.5 [dd, ^1J(C,P) = 43.2, 39.7 Hz, CC(CH$_3$)$_3$]; ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 147.1, 250.0 [each d, ^2J(P,P) = 27.13 Hz]; MS (70 eV, EI): m/z (%): 297 (100) $[M]^+$, 214 (17) $[M-C_6H_{11}]^+$, 200 (2) $[M-C_6H_{11}N]^+$; $C_{16}H_{29}NP_2$ (297.36).

General procedure for the preparation of the 1,3,5-triphosphabenzenes 8a–e: Four equivalents **1a–e** were added at −78 °C to a solution of **9a** in toluene. After the mixture was allowed to warm up, toluene was distilled off at 20 °C at 10^{-2} mbar, the residue was redissolved in *n*-pentane, and purified by column chromatography on silica gel (deactivated with 4% water, column: 20 × 2.0 cm). The yellow fraction afforded **8a–e** after removal of the solvent. In the cases of **8a–c** no further purification was necessary, **8d** and **8e** were recrystallized from *n*-pentane.

2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene (8a): Compound **9a** (100 mg, 0.47 mmol) in toluene (5 mL) and **1a** (180 mg, 1.8 mmol) produced **8a** (120 mg, 68%) as a yellow powder. ^{1}H NMR ([D$_8$]THF, 400 MHz, 25 °C): δ = 1.34 [s, 27H, C(CH_3)$_3$]; ^{13}C NMR ([D$_8$]THF, 100.6 MHz, 25 °C): δ = 36.1 [X part of A$_2$BX spin system, $|J$(P,P)$|$ = 8.0 Hz, ^3J(C,P) = 14.5 Hz, ^5J(C,P) = 1.1 Hz, ($\nu_A-\nu_B$) = 0.1 Hz, C(CH$_3$)$_3$], 44.53 [X part of A$_2$BX spin system, $|J$(P,P)$|$ = 8.1 Hz, ^2J(C,P) = 24.5 Hz, ^4J(C,P) = 1.6 Hz, ($\nu_A-\nu_B$) = 0.7 Hz, C(CH$_3$)$_3$], 211.8 [X part of A$_2$BX spin system, $|J$(P,P)$|$ = 8.0 Hz, ^1J(C,P) = 77.0 Hz, ^3J(C,P) = 15.2 Hz, ($\nu_A-\nu_B$) = 10.2 Hz, ring C]; ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 232.6 (s); MS (70 eV, EI): m/z (%): 300 (39) $[M]^+$, 169 (100) $[M-C_5H_9P_2]^+$, 100 (32) $[M-C_{10}H_{18}P_2]^+$; $C_{15}H_{27}P_3$ (300.30).

2,4,6-Tris(1-adamantyl)-1,3,5-triphosphabenzene (8b): Compound **9a** (140 mg, 0.60 mmol) in toluene (3 mL) and **1b** (428 mg, 2.4 mmol) in toluene (3 mL) produced **8b** (150 mg, 36%) as a yellow powder. ^{1}H NMR (C$_7$D$_8$, 400 MHz, 25 °C): δ = 1.75 [m, 18H, CH_2], 2.13 [m, 9H, CH], 2.48 [m, 18H, CH_2]; ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz, 25 °C): δ = 30.4 [s, CH], 37.0 [s, CH_2], 38.7 [X part of A$_2$BX spin system, $|J$(P,P)$|$ = 5.9 Hz, ^3J(C,P) = 15.5 Hz, ^5J(C,P) = 1.0 Hz, ($\nu_A-\nu_B$) = 0.1 Hz, CH$_2$], 46.5 [X part of A$_2$BX spin system, $|J$(P,P)$|$ = 6.0 Hz, ^2J(C,P) = 22.0 Hz, ^4J(C,P) = 1.5 Hz, ($\nu_A-\nu_B$) = 0.8 Hz, adamantyl-C], 212.2 [X part of A$_2$BX spin system, $|J$(P,P)$|$ = 5.9 Hz, ^1J(C,P) = 77.5 Hz, ^3J(C,P) = 15.5 Hz, ($\nu_A-\nu_B$) = 10.2 Hz, ring-C]; ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 238.1 (s); MS (70 eV, EI): m/z (%): 534 (21) $[M]^+$, 325 (100) $[M-C_{11}H_{15}P_2]^+$; $C_{33}H_{45}$ P$_3$ (534.64).

2,4,6-Tris(1,1-dimethylpropyl)-1,3,5-triphosphabenzene (8c): Compound **9a** (305 mg, 1.34 mmol) in toluene (3 mL) and **1c** (612 mg, 5.36 mmol) produced **8c** (271 mg, 59%) as an orange-yellow oil. ^{1}H NMR (CDCl$_3$, 200 MHz, 25 °C): δ = 0.84 [t, ^3J(H,H) = 7.4 Hz, 9H, CH$_2$CH_3], 1.74 [s, 18H, C(CH_3)$_2$C$_2$H$_5$], 2.14 [q, ^3J(H,H) = 7.4 Hz, 6H, CH_2CH$_3$]; ^{13}C NMR (CDCl$_3$, 50.3 MHz, 25 °C): δ = 9.2 [s, CH$_2$CH_3], 32.7 [m, C(CH_3)C$_2$H$_5$], 40.5 [m, CH$_2$CH$_3$], 46.9 [m, C(CH$_3$)C$_2$H$_5$], 208.8 [m, ring C][25]; ^{31}P NMR (CDCl$_3$, 81.0 MHz, 25 °C): δ = 238.8 (s); MS (70 eV, EI): m/z (%): 342 (31) $[M]^+$, 197 (100) $[M-C_6H_{11}P_2]^+$, 114 (9) $[C_6H_{11}P]^+$; elemental analysis calcd for $C_{18}H_{33}P_3$ (342.38): C 63.15, H 9.71; found C 63.13, H 10.1.

2,4,6-Tris(1-methylcyclopentyl)-1,3,5-triphosphabenzene (8d): Compound **9a** (313 mg, 1.37 mmol) in toluene (3 mL) and **1d** (691 mg, 5.48 mmol) produced **8d** (192 mg, 37%) as a yellow powder. ^{1}H NMR (CDCl$_3$, 200 MHz, 25 °C): δ = 1.54 [s, 9H, CH_3], 1.78–1.94 [m, 12H, CH_2], 2.24–2.42 [m, 12H, CH_2]; ^{13}C NMR (CDCl$_3$, 100.6 MHz, 25 °C): δ = 22.9 [s, cyclopentyl-CH$_2$], 35.4 [m, CH$_3$], 42.3 [m, cyclopentyl-CH$_2$], 55.6 [m, C(CH$_2$)$_2$CH$_3$], 211.8 [m, ring C][25]; ^{31}P NMR (CDCl$_3$, 81.0 MHz, 25 °C): δ = 234.2 (s); MS (70 eV, EI): m/z (%): 378 (33) $[M]^+$, 221 (100) $[M-C_7H_{11}P_2]^+$, 126 (15) $[C_7H_{11}P]^+$; elemental analysis calcd for $C_{21}H_{33}$ P$_3$ (378.42): C 66.65, H 8.79; found C 66.5, H 9.0.

2,4,6-Tris(1-methylcyclohexyl)-1,3,5-triphosphabenzene (8e): Compound **9a** (209 mg, 0.92 mmol) in toluene (2 mL) and **1e** (516 mg, 3.68 mmol) produced **8e** (170 mg, 44%) as a yellow powder. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 25 °C): δ = 1.36–1.74 [m, 18H, CH_2], 1.65 [s, 9H, CH_3], 2.05–2.11 [m, 6H, CH_2], 2.81–2.88 [m, 6H, CH_2]; ^{13}C NMR (C$_6$D$_6$, 100.6 MHz, 25 °C): δ = 23.2 [s, cyclohexyl-CH$_2$], 26.6 [s, cyclohexyl-CH$_2$], 35.8 [m, CH$_3$], 41.6 [pseudo t, ^3J(C,P) = 16.2 Hz, cyclohexyl-CH$_2$], 47.6 [pseudo-t, ^2J(C,P) = 19.5 Hz, C(CH$_2$)$_2$CH$_3$], 212.1 [m, ring C][25]; ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 242.8 (s); MS (70 eV, EI): m/z (%): 420 (18) $[M]^+$, 249 (100) $[M-C_8H_{13}P_2]^+$, 140 (7) $[C_8H_{13}P]^+$; $C_{24}H_{39}P_3$ (420.50).

2,4-Bis(1-adamantyl)-6-*tert*-butyl-1,3,5-triphosphabenzene (21): Compound **1a** (59 mg, 0.59 mmol) was added at −78 °C to a solution of **9a** (140 mg, 0.59 mmol) in toluene (5 mL) and the mixture was then allowed to warm to room temperature. After cooling back to −78 °C a solution of **1b** (320 mg, 1.77 mmol) in toluene (2 mL) was added and the mixture was allowed to warm up. The solvent was distilled off under reduced pressure (20 °C at 10^{-2} mbar). The residue was redissolved in *n*-pentane and purified by column chromatography on silica gel (deactivated with 4% water, column: 20 × 2.0 cm). The yellow fraction (210 mg) was found to contain **21** contaminated by traces of **8b**. ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 237.0, 237.2 [AB$_2$ spin system, ^2J(P,P) = 6.2 Hz]; MS (70 eV, EI): m/z (%): 456 (5) $[M]^+$, 325 (100) $[M-C_5H_9P_2]^+$; $C_{27}H_{39}P_3$ (456.53).[26]

6-(1-Adamantyl)-2,4-di-*tert*-butyl-1,3,5-triphosphabenzene (22): A solution of **1b** (120 mg, 0.66 mmol) in toluene (3 mL) was added at −78 °C to a solution of **9a** (150 mg, 0.66 mmol) in toluene (5 mL), and the mixture was then allowed to warm to room temperature. After cooling back to −78 °C **1a** (200 mg, 2.00 mmol) was added and the mixture allowed to warm up again. The solvent was distilled off under reduced pressure (20 °C at 10^{-2} mbar). The residue was redissolved in *n*-pentane and purified by column chromatography on silica gel (deactivated with 4% water, column: 20 × 2.0 cm). The yellow fraction (200 mg) was found to contain **22** contaminated by traces of **8a**. ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 25 °C): δ = 235.2, 235.4 [AB$_2$ spin system, ^2J(P,P) = 7.9 Hz]; MS (70 eV, EI): m/z (%): 378 (14) $[M]^+$, 169 (100) $[M-C_{11}H_{15}P_2]^+$; $C_{21}H_{33}P_3$ (378.42).[26]

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[26] The experimental data (^{31}P/MS) were determined from the unseparable mixtures of **21**/**8b** and **22**/**8a**.

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