Organophosphorus Compounds, Part 146*
Imidovanadium(V) Complexes as Reaction Partners for Kinetically Stabilized Phosphaalkynes. Synthesis and Reactivity of 3-Aza-1,2,4,6-tetraphospha-quadricyclanes

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Cyclooligomerization of Phosphaalkynes, Imidovanadium(V) Complexes, 3-Aza-1,2,4,6-tetraphospha-quadricyclanes

The Lewis base adducts of imidovanadium(V) compounds **5a,b** undergo chemoselective cyclooligomerization reactions with the kinetically stabilized phosphaalkynes **4a-e** to furnish the azatetraphosphaquadricyclanes **6a-f** with incorporation of the imido fragment. The reactivity of this novel class of heteropolycyclic compounds has been examined exemplarily for compound **6a**. Complexation of one and two phosphorus atoms was achieved by reaction with nonacarbonyldiiron or the tungsten pentacarbonyl-THF complex resulting in the formation of the transition metal compounds **17-20**. Reactions of **6a** with the sulfonyl azides **21a-c** furnished the *Staudinger* products **22a-c**. The reaction of **6a** with two equivalents of tosyl azide gave a surprising result. No double complexation leading to a symmetrical product was achieved, and compound **23** was obtained instead in which the two phosphorus atoms of one diphosphirane ring are functionalized. Oxidative cleavage of a P/P bond in **6a** to furnish product **24** is observed in the reaction of **6a** with the Lewis base-free imidovanadium(V) species **15a**.

Introduction

Cage compounds, some of which have highly symmetrical skeletons, have always been of great interest to chemists. Their often tedious, multistage syntheses have presented a challenge to experimental techniques and the unusual bonding relationships have generated new impulses for theoretical considerations.

Thus, it is not surprising that the construction of phosphorus-carbon cage compounds has developed into an important field in the chemistry of kinetically stabilized phosphaalkynes. In contrast to their all-carbon analogues, however, access to the phosphorus-carbon cage systems has only become possible in the past ten years with the phosphaalkynes being indispensable starting compounds.

Major breakthroughs in this development include the syntheses of the tetraphosphacubane **1** [1], the tetraphosphabishomoprismane **2** [2], and the hexaphosphapentaprismane **3** [3] (Scheme 1). The cubane **1** was of particular interest on account of its high symmetry and its at first inexplicable spectral properties. Accordingly, the remarkably stable cubane **1** has, on the one hand, been the subject of numerous theoretical bonding studies [4–6] and, on the other hand, the starting point for many functionalization reactions at the phosphorus atoms [7–9]. Although the first syntheses of the phosphaalkyne tetramers **1** and **2** were based on the thermolysis of the *tert*-butylphosphaalkyne **4a**, many novel synthetic strategies have since been developed for the specific construction of polycyclic phosphorus-carbon systems. These now provide selective and high-yield access to the cage compounds **1** and **2**. The synthetic principles employed include transition metal- (→ **1** [10,11]), base- (→ **2** [12]), and Lewis acid-mediated processes (→ **3** [3]).

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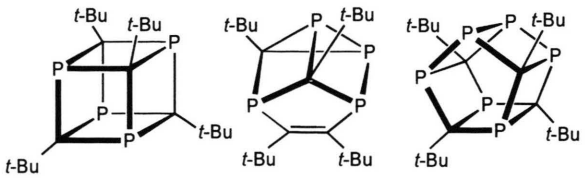
In this context we posed the question of whether and how the kinetically stabilized phosphaalkynes would react with imidovanadium(V) compounds which possess Lewis acid character. We expected that the enormous cyclooligomerization potential of the phosphaalkynes would result in the formation of oligomeric phosphorus-carbon compounds.



Scheme 1

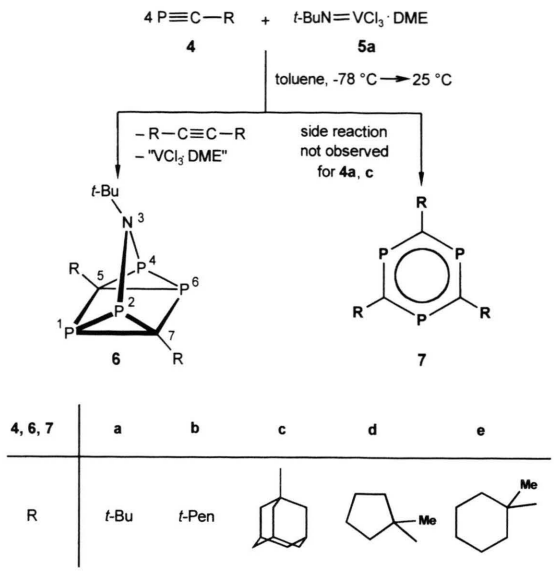
In the present article we describe the selective synthesis of the 3-aza-1,2,4,6-tetraphosphaquadricyclanes **6**, formed by cocyclooligomerization of the phosphaalkynes **4** proceeding with concomitant incorporation of the imido fragment of the vanadium compound and cleavage of two RC fragments (→ alkynes).

Results and Discussion

Formation of azatetraphosphaquadricyclanes

The reactions of the phosphaalkynes **4a-e** with the imidovanadium(V) compound **5a** in a molar ratio of 4:1 furnished the yellow azatetraphosphaquadricyclanes **6a-e** rather selectively in yields of 47–76% [13]. The corresponding 1,3,5-triphosphabenzenes [14] **7b,d,e** (1–3%) were formed as by-products only in the reactions of the phosphaalkynes **4b**, **4d**, and **4e** (Scheme 2).

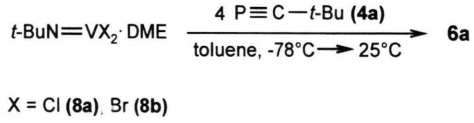
The structure elucidation of compounds **6** from the NMR data is discussed for the example of product **6a**: The four phosphorus atoms of the tetracyclic system give rise to the signals of an AA′XX′ spin system centered at δ = −7.4 (P2, P4) and −123.0 (P1, P6). Although the signals in the A part of the spectrum are strongly broadened on account of the proximity of the ^{14}N atom (I = 1), coupling constants in the range from 2.1 to 161.1 Hz can be derived from the X part. The ^1H NMR spectrum supports this interpretation; the two *t*-butyl groups at C-5 and C-7 give a doublet signal at δ = 1.00 with a $^4J_{H,P}$ coupling of 1.2 Hz, while the signal of the *t*-butyl group at nitrogen appears



Scheme 2

at δ = 1.53 as a triplet with a $^4J_{H,P}$ coupling of 0.9 Hz. The $^{13}C\{^1H\}$ NMR spectrum contains the signals for the *t*-butyl groups as well as a multiplet at δ = 30.3 for the skeletal carbon atoms C-5 and C-7 which cannot be distinguished.

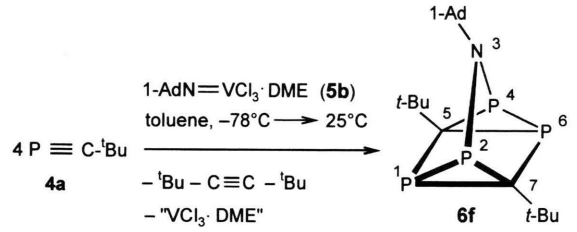
The structure proposed for **6a** is in harmony with these NMR data and was confirmed by single crystal X-ray crystallography [13].



Scheme 3

In order to examine the dependence of the reaction on the oxidation state of the imidovanadium compound, the phosphaalkyne **4a** was allowed to react with the imidovanadium(IV) complexes **8a** and **8b** [15] (Scheme 3). In analogy to the reaction with the vanadium(V) compound **5a** selective formation of the cage compound **6a** was observed.

Variation of the substituent at nitrogen in the imidovanadium(V) complex also enabled the substitution pattern of the tetracyclic product to be changed. Thus, reaction of the *N*-1-adamantyl substituted vanadium compound **5b** with four equivalents of **4a** furnished the azatetraphosphaquadricyclane **6f** together with a small amount of the triphosphabenzene **7a** as a by-product (Scheme 4).



Scheme 4

Apart from the signals of the different substituents at nitrogen (1-adamantyl in place of *t*-butyl) the NMR data of **6f** were in good agreement with those of **6a**.

A plausible mechanism for the formation of the azatetraphosphaquadricyclanes **6** can be proposed because ^{31}P and ^{51}V NMR spectroscopic monitoring of the reaction of **4a** with **5a** (no by-product **7a**!) reveals the presence of the three intermediates **9**, **11**, and **12**. When the DME adduct **5a** is allowed to react with only one equivalent of **4a** the specific formation of the metallacyclic species **9a** is observed by NMR spectroscopy (Table 1); however, its isolation after removal of the solvent is not possible (see below). When the compounds **4a** and **5a** are allowed to react in a molar ratio of 2:1, an inseparable mixture of **6a** and the previously unknown 1,2,5-azadiphosphole **11a**, characterized unambiguously by NMR spectroscopy, is obtained. Recently Nixon and coworkers [16] have described the synthesis and crystal structure of the 1,2,5-azadiphosphole (**11a**) complex [Ir(η^5-Cp*)(η^4-{^{t}BuCPNtBuPCtBu})] starting from [IrCp*(N^{t}Bu] on treatment with an excess of **4a**. Attempts to displace **11a** from iridium have proved unsuccessful. Convincing evidence that **11a** is an intermediate on the way to the quadricyclane is provided by the addition of further phosphaalkyne **4a** to a mixture of **6a** and **11a**. In this case **11a** reacts as expected to give **6a** which at the same time excludes the further participation of transition metal fragments in the following reaction steps. NMR spectroscopic monitoring reveals that the formation of **6a** proceeds by way of the intermediate **12a** (Fig. 1) which, however, cannot be isolated on account of its limited stability. These experimental observations allow the following mechanism for the formation of the quadricyclanes to be proposed (Scheme 5).

Table 1. Characteristic ^{51}V and ^{31}P NMR data of 1,2,4-azaphosphavanada(V)cyclobutene **9*** and **16a**.

Compound	$\delta(^{51}V)$ [ppm]	$W_{1/2}$ [Hz]	$\delta(^{31}P)$ [ppm]
DME complex (**9a**)*	+307	367	–73.0
PMe_3 complex*	+308	460	–68.4 +30.9 (coord. PMe_3)
PPh_3 complex*	+306	320	–72.9 +36.3 (coord. PPh_3)
16a [14]	+310	209	–73.0

* Unstable intermediate.

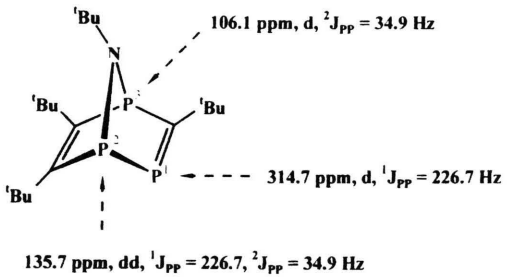
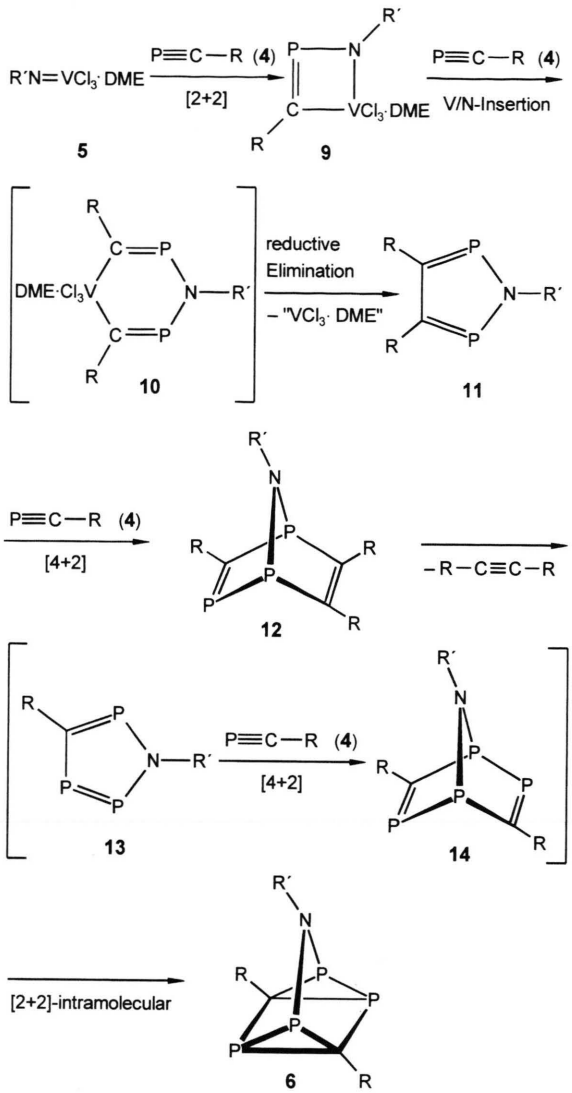


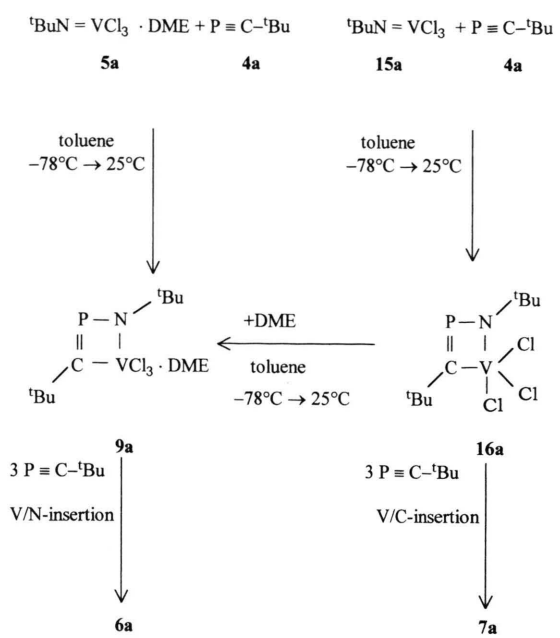
Fig. 1. $^{31}P\{^1H\}$NMR data (C_6D_6) of the unstable azatriphosphanorbornadiene **12a**, obtained by direct NMR spectral monitoring of the reaction of **4a** with **5a**.

The unstable four-membered metallacyclic species **9** is formed in a [2+2] cycloaddition between the DME adduct **5** and the phosphaalkyne **4**. After insertion of a second equivalent of **4** into the V/N bond a formal ring expansion to afford the six-membered metallacyclic species **10** occurs. The subsequent reductive elimination of the transition metal fragment, detected in the residue as $VCl_3 \cdot 1.5$ DME, furnishes the 1,2,5-azadiphosphole **11**. In the following reaction step **11** undergoes a [4+2] cycloaddition with a third equivalent of **4** to give the azatriphosphanorbornadiene **12** which dissociates in a retro-Diels-Alder reaction to liberate the dialkylacetylene and the azatriphosphole **13**. In the case of the 1-adamantylphosphaalkyne **4c** bis(1-adamantyl)acetylene can be isolated and identified by comparison with literature data [17]. The final steps of the sequence comprise a further [4+2] cycloaddition with a fourth equivalent of the phosphaalkyne. The resultant azatetraphosphanorbornadiene **14** then undergoes stabilization by way of an intramolecular, head-to-tail cycloaddition of the two phosphaalkene units [1, 2] to form the tetracyclic system **6**.

Equimolar amounts of phosphaalkyne **4a** and the Lewis base-free imidovanadium(V) trichloride



Scheme 5



Scheme 6

15a furnish the stable and isolable 1,2,4-azaphosphavanada(V)cyclobutene **16a**; on reaction with an excess of **4a** the 1,3,5-triphosphabenzene **7a** is formed by a catalytic process [14]. The good agreement of the ^{31}P and ^{51}V NMR data for **16a** and **9a** (Table 1) supports the proposed four-membered ring structure of **9a** which unlike **16a** undergoes decomposition (no identifiable products) and can be merely detected as an unstable intermediate by NMR spectroscopy. When **16a** is allowed to react with one equivalent of DME, **9a** is formed furnishing the quadricyclane **6a** on addition of **4a**, while in the absence of DME triphosphabenzene **7a** is formed (Scheme 6). The specific formation of **6a** or **7a** via **9a** or **16a** is observed only for *t*-butyl as a substituent of the imidovanadium(V) compound and the phosphaalkyne; changes in the alkyl group afford triphosphabenzene **7** and quadricyclane **6** as by-products indicating that both 1,2,4-azaphosphavanada(V)cyclobutene rings **9** and **16** can react with phosphaalkyne by V/N- and V/C-insertion at a time in one way selectively. Starting from $^tBuN{=}VCl_3 \cdot PR_3$ (R = Me, Ph) [18] and one equivalent of **4a,** the corresponding metallacycles **9** (Table 1) are formed, which are unstable and produce 1,2,5-azadiphosphole **11a** and quadricyclane **6a** by decomposition.

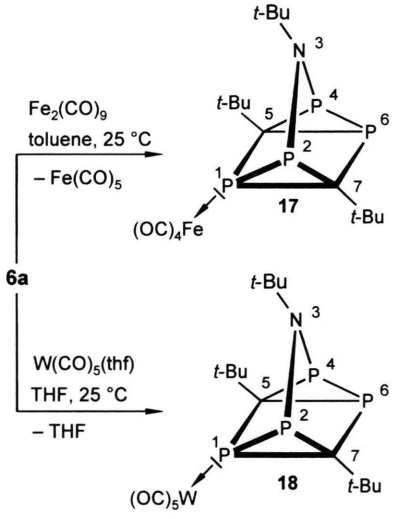
Studies on the Reactivity of the Azatetraphosphaquadricyclane 6a

In addition to the synthesis of the title compounds we were also interested in their reactivity. The tetracyclic compounds **6** possess four $\lambda^3\sigma^3$-phosphorus atoms with a predisposition for functionalization reactions. Thus, we investigated the ability of the polycyclic compound **6a**, which is preparatively the most easily accessible, to func-

tion as a phosphane ligand in transition metal complexes.

Complexation of **6a** *with diiron nonacarbonyl and the tungsten pentacarbonyl-THF complex*

The reactions of the azatetraphosphaquadricyclane **6a** with diiron nonacarbonyl in toluene, or tungsten pentacarbonyl-THF complex in tetrahydrofuran, in a molar ratio of 1:1 afforded the η^1-complexes **17** or **18**. Although the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures reveal the presence of the starting material **6a** together with the respective singly and doubly (see below) complexed tetracyclic species, chromatographic work-up and subsequent crystallization from pentane selectively furnishes the pure complexes **17** or **18** (Scheme 7).



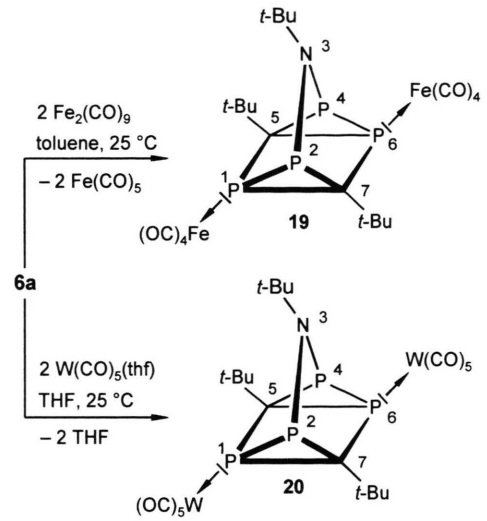
Scheme 7

Elemental analytical and mass spectral data clearly demonstrate the formation of the complexes **17** and **18** from one molecule of **6a** and a 16-valence electron metal fragment. In accord with the unsymmetrical structures of the complexes **17** and **18**, their $^{31}P\{^1H\}$ NMR spectra each contain four signals with the complexation effecting only minor changes in the chemical shifts in comparison to the uncomplexed starting material **6a**. An exception is the signal of the complexed phosphorus atom P-1 in the iron complex **17** which experiences a significant shift to low field (δ = −40.7). Furthermore, the signal for the tungsten-complexed phosphorus atom P-1 in compound **18** at δ = −104.1 exhibits typical tungsten satellite lines with a $^1J_{P,W}$ coupling of 222.3 Hz. This signal appears as a double pseudotriplet as a result of a $^1J_{P,P}$ coupling of 151.7 Hz and two equally sized $^2J_{P,P}$ couplings of ~6 Hz. As expected, the ^1H NMR spectra contain three signals each for the *t*-butyl groups of compounds **17** and **18** with characteristic chemical shifts. The $^{13}C\{^1H\}$ NMR spectra also support the retention of the quadricyclane structure. When the chemical shifts of the carbon signals of **17** and **18** are compared with those of the starting material **6a**, it is seen that the skeletal carbon atoms C-5 and C-7 experience a marked paramagnetic shift from δ = 30.3 (**6a**) to values of δ = 36.5 – 40.0. In addition to the more or less unchanged positions of the signals for the carbon atoms of the *t*-butyl groups, there are also the expected signal patterns for the carbon atoms of the carbonyl groups bound to the respective metal. While the carbonyl ligands of compound **17** give rise to only one signal at low field (δ = 217.3), the carbon atoms of the carbonyl ligands in compound **18** produce separate signals for the axial (δ = 197.8) and the equatorial (δ = 196.8) ligands.

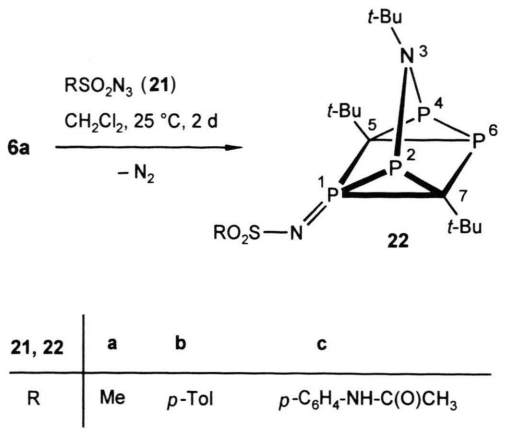
Two-fold complexation of **6a**

When **6a** was allowed to react with diiron nonacarbonyl or, respectively, tungsten pentacarbonyl-THF complex in a molar ratio of 1:2, the doubly complexed tetracyclic species **19** or **20** were formed (Scheme 8).

The 1:2 composition of the products **19** and **20** from one molecule of the quadricyclane **6a** and two parts of the transition metal fragment is clearly apparent from elemental analytical and mass spectral data. In accord with the symmetrical coordination of **6a** by two of the respective transition metal carbonyl fragments, the $^{31}P\{^1H\}$ NMR spectra of **19** and **20** reveal splitting patterns analogous to the signals of **6a** although the resonances of **19** and **20** occur at lower field than those of **6a**. The shift to lower field is larger for the iron-complexed phosphorus atoms. Thus, the signals for the complexed phosphorus atoms P-1/P-6 are seen at δ = −43.9 (**19**) and δ = −111.9 (**20**) [compared with δ = −122.7 (**6a**)] and those for P-2/P-4 are found at δ = 19.6 (**19**) and δ = 21.7 (**20**) [compared with δ = −7.1 (**6a**)]. The $^{13}C\{^1H\}$ NMR spectra of



Scheme 8



21, 22	a	b	c
R	Me	*p*-Tol	*p*-C_6H_4-NH-C(O)CH_3

Scheme 9

19 and **20** also reflect their symmetrical structures. As expected, the chemical shifts of the skeletal carbon atoms C-5 and C-7 are most affected by the complexation. In contrast to these low field shifts for C-5 and C-7 of δ = 44.5 and δ = 41.9, respectively, for **19** and **20** as compared to δ = 30.3 for **6a**, the signals for the *t*-butyl groups are practically unchanged.

Although these single and double complexations of **6a** can be realized at room temperature, three- and four-fold complexations have not yet been achieved.

Simple Staudinger reactions of **6a** *with the sulfonyl azides* **21a-c**

The *Staudinger* reaction [19] of phosphanes with organic azides to produce phosphane imines also plays a significant role in the chemistry of phosphorus-carbon cage compounds. Thus, for example, the tetraphosphacubane **1** has been singly and doubly functionalized by means of the *Staudinger* reaction [20,21]. Thus, it was of interest to examine the behavior of *t*-butylquadricyclane **6a** under the conditions of the *Staudinger* reaction.

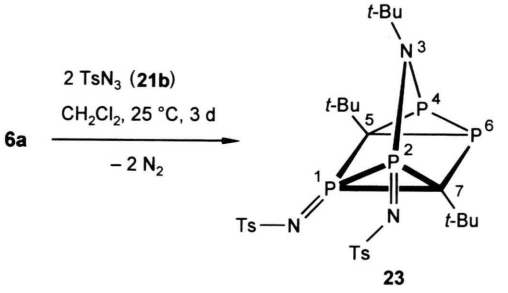
Reactions of **6a** with an equimolar amount of the sulfonyl azides **21a-c** resulted in the selective formation of the *Staudinger* products **22a-c** (Scheme 9).

The mass spectral data and a correct elemental analysis for **22b** clearly demonstrate the formation of the polycyclic species **22a-c** from one equivalent of the quadricyclane **6a** and one equivalent of the respective sulfonyl azide **21a-c** with loss of a molecule of nitrogen. Owing to the formation of the monophosphane imines the $^{31}P\{^1H\}$ NMR spectra of compounds **22a-c** in each case reveal four signal groups indicative of an unsymmetrical structure. As a result of the deshielding effect of the doubly bonded nitrogen, the signals of phosphorus atoms P-1 experience a dramatic shift to lower field in comparison to the corresponding signal of the staring material **6a** and appear at δ = 198.6–203.2. The signals of the phosphorus atom P-2 at δ = 130.8–133.9 are also markedly shifted by *ca.* 140 ppm to lower field. The two signal groups in the high field region at δ = –19.6 to –22.2 for P-4 and at δ = –142.7 to –146.7 for P-6 are suggestive of an intact diphosphirane unit that is not appreciably influenced by the functionalization. In contrast, the coupling constants in the functionalized diphosphirane unit reveal a characteristic feature, namely the drastic reduction in magnitude of the direct $^1J_{P,P}$ coupling constants between P-1 and P-2 from 161.0 Hz in **6a** to 4.5 – 6.1 Hz in the *Staudinger* products **22a-c**. Besides the typical signals for the imino substituents and the *t*-butyl groups the $^{13}C\{^1H\}$ NMR spectra each contain two separate signals for the skeletal carbon atoms C-5 and C-7 that experience strong paramagnetic shifts and appear between δ = 43.5 and 50.1.

With less electrophilic azides such as alkyl or aryl azides, on the other hand, the azatetraphosphaquadricyclane **6a** does not show any tendency to form the corresponding phosphane imines even under drastic reaction conditions.

Twofold Staudinger reaction of **6a** *with tosyl azide* (**21b**)

When the reaction between **6a** and tosyl azide (**21b**) was performed in a 1:2 molar ratio the doubly functionalized azaquadricyclane **23** was obtained after crystallization as a pale yellow powder in 74% yield (Scheme 10).



Scheme 10

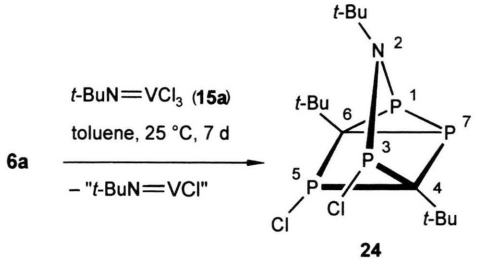
The EI mass spectrum clearly reveals the formal composition of **23** originating from one molecule of the tetracyclic starting material **6a** and two molecules of tosyl azide (**21b**) with loss of two molecules of nitrogen.

The $^{31}P\{^1H\}$ NMR spectrum of product **23** contains a total of four signal groups indicative of an unsymmetrical structure. Thus, the occurrence of the second functionalization at P-6 – as is the case for the second complexation – can be discounted. In principle, the spectral data are compatible with a functionalization at P-2 or P-4. However, when the spin systems are analyzed a $^1J_{P,P}$ coupling constant of 172.9 Hz is found and this unambiguously demonstrates that one diphosphirane unit has been functionalized. Since in "simple" *Staudinger* products the direct $^1J_{P,P}$ coupling decreases dramatically, it can be deduced with certainty that the second *Staudinger* reaction has occurred at P-2. The positions of the phosphorus signals are strongly shifted in comparison to those of the monofunctionalized product **22b**. While the signal of the primarily functionalized phosphorus atom P-1 is shifted by *ca.* 45 ppm to higher field and appears at δ = 155.5, the signal of phosphorus atom P-2 experiences an appreciably larger shift to higher field of *ca.* 115 ppm and is found at δ = 15.0. Only the chemical shift of the signal for P-6 remains more or less unchanged at δ = –147.4 in comparison to that of **22b**, whereas the signal for P-4 is subject to a paramagnetic shift of about 50 ppm to δ = 26.2. With the exception of the signals for the second substituent and the $^{13}C\{^1H\}$ chemical shifts of the skeletal carbon atoms which are markedly shifted to higher field and appear at δ = 36.6 and 37.4, the ^1H and $^{13}C\{^1H\}$ NMR data are in good agreement with those of compound **22b**.

Although the single and double functionalizations of **6a** by the *Staudinger* reaction can be realized at 25 °C, higher degrees of functionalization (three- and four-fold) of the azatetraphosphaquadricyclane **6a** cannot be achieved through reaction with sulfonyl azides.

Oxidative P/P bond cleavage in the quadricyclane **6a**

The reaction of ^{t}BuN=VCl$_3$ (**15a**) with PR$_3$ (R = Me, Ph) yields the stable phosphane complexes [^{t}BuN=VCl$_3$·PR$_3$] [18]. When the quadricyclane **6a** was allowed to react with an equimolar amount of **15a** for one week, no phosphane complex analogous to **17**, **18** could be isolated, but the tricyclic compound **24** was formed (Scheme 11). Excessive **15a** does not lead to an oxidative cleavage of the remaining P/P-bond in compound **24**.



Scheme 11

The construction of **24** from the quadricyclane **6a** and two chlorine atoms is unambiguously demonstrated by its mass spectral data. The isotope pattern of the molecular ion peak at *m/z* = 403 in the EI mass spectrum confirms the incorporation of the two chlorine atoms in the product.

Evaluation of the spin systems in the $^{31}P\{^1H\}$ NMR spectrum clearly shows that one P/P bond in the tetracyclic compound **6a** has been cleaved and the respective phosphorus atoms chlorinated under the action of **15a**. While the signals of the phosphorus atoms P-1 and P-7 appear at $\delta = -9.1$ (P-1) and -112.3 (P-7) with only minor shifts in comparison to the corresponding signals for the starting compound **6a**, the signals for the phosphorus atoms P-3 and P-5 are markedly shifted to lower field and now appear at $\delta = 225.5$ (P-3) and 93.9 (P-5). These drastic shifts to lower field of more than 200 ppm are well known and are always observed when a P/P bond in a diphosphirane increment is cleaved with concomitant halogenation of the respective phosphorus atoms [21,22]. The observed splitting patterns of the phosphorus signals are compatible only with the proposed constitution for compound **25**. Thus, the signals of the phosphorus atoms P-1 and P-7 of the retained diphosphirane unit appear as double doublets of doublets on account of their coupling to three other phosphorus atoms each, while the chlorinated phosphorus atoms P-3 and P-5 give rise to double doublet signals as a result of the absence of the direct $^1J_{P,P}$ coupling.

Experimental Section

All reactions were performed under argon (purity > 99,998%; BTS catalyst, molecular sieve 5Å) using Schlenk techniques. The solvents were dried by standard procedures, distilled, and stored under argon until used. Column chromatography was performed with a positive pressure of argon on the column. Silica gel and alumina were heated (175 °C) for 12 h under vacuum and then deactivated with 4% water saturated with argon (Brockmann activity II). Melting points are uncorrected (heating rate 2°/min). NMR (1H, 13C, 31P, 51V): Bruker AC 200 and AMX 400; δ in ppm (298K) referenced to TMS (internal), 85% H_3PO_4 (external), $VOCl_3$ (external). MS: Finnigan MAT 90. IR: Perkin Elmer FT-IR 16 P C. Starting Compounds **4a**,**c** [23], **4b** [24], **4d**,**e** [**25**,**26**], **5a**,**b** [27,28], **21a** [29], **21b** [30] and **15a** [31] were prepared by published methods.

3,5,7-Tri-tert-butyl-3-aza-1,2,4,6-tetraphosphatetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**6a**)

To a stirred solution of **5a** (0.32 g, 1.00 mmol) in 5 ml of toluene was added at −78 °C compound **4a** (0.40 g, 4.00 mmol). Subsequently the reaction mixture was allowed to warm to 25 °C and stirred for 12 h. After removal of the solvent under vacuum, the residue was chromatographed over alumina. The first yellow fraction (*n*-pentane) was collected and evaporated to dryness. The resultant yellow solid was recrystallized from *n*-pentane at −78 °C to yield the pure product **6a** as pale yellow crystals (0.25 g, 76%): m.p. 76–77 °C.

$^{31}P\{^1H\}$ NMR (C_6D_6): −123.0, −7.4 [AA′XX′ spin system, $J_{P,P}$(AX, A′X′) = 163.7, $J_{P,P}$(AA′) = 22.3, $J_{P,P}$(XX′) = 5.7, $J_{P,P}$(A′X, AX′) = 2.3 Hz]. ^1H NMR (C_6D_6): 0.99 (d, $J_{H,P}$ = 1.2 Hz, 18H), 1.53 (t, $J_{H,P}$ = 0.9 Hz, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 28.8–31.7 (m), 30.1 (m_c), 32.1 (m_c), 34.0 (t, $J_{C,P}$ = 10.6 Hz), 56.8 (t, $J_{C,P}$ = 14.4 Hz). MS (EI, 70 eV): *m/z* (%) = 333 (63) [M^+], 177 (100). – $C_{14}H_{27}NP_4$ (333.26): calcd. C 50.45, H 8.16, N 4.20; found C 50.5, H 8.2, N 4.2.

5,7-Di(1-adamantyl)-3-tert-butyl-3-aza-1,2,4,6-tetraphosphatetracyclo[3.2.0.0^{2,7}.0^{4,6}]-heptane (**6b**)

To a stirred solution of **5a** (0.32 g, 1.00 mmol) in 5 ml of toluene was added at −78 °C a solution of **4b** (0.68 g, 4.00 mmol) in 2 mL of toluene. Subsequently the reaction mixture was allowed to warm to 25 °C and stirred for 24 h. After removal of the solvent under vacuum, the residue was chromatographed over alumina. The first yellow fraction (*n*-pentane) was collected and evaporated under vacuum. The resultant yellow residue consisting mainly of **6b** and bis(1-adamantyl)acetylene was separated by bulb-to-bulb distillation (140 °C/10^{-2} mbar) to give **6b** as a yellow solid. Crystallization from *n*-pentane at −78 °C afforded a pale yellow powder (0.14 g, 34%).

$^{31}P\{^1H\}$ NMR (C_6D_6): −129.3, −14.9 [AA′XX′ spin system, $J_{P,P}$(AX, A′X′) = 162.5, $J_{P,P}$(AA′) = 22.6, $J_{P,P}$(XX′) = 4.7, $J_{P,P}$(A′X, AX′) = 1.7 Hz]. ^1H NMR (C_6D_6): 1.42–1.96 (m, 30H), 1.66 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 28.7 (s), 30.0–32.9 (m), 33.2 (m_c), 34.1 (t, $J_{C,P}$ = 10.5 Hz), 36.8 (s), 43.3 (m_c), 56.8 (t, $J_{C,P}$ = 14.4 Hz). MS (EI, 70 eV): *m/z* (%) = 489 (50) [M^+], 335 (100). HRMS: calcd 489.2033, found 489.2004.

General procedure for the preparation of the 3-aza-1,2,4,6-tetraphosphaquadricyclanes **6c-e**

To a solution of **5a** (0.32 g,1.00 mmol) in 5 ml of toluene the phosphaalkynes **4c**, **4d**, or **4f** (4.00 mmol) were added at −78 °C, the reaction mixtures allowed to warm to 25 °C and stirred for 48 h (168 h in the case of **4f**). The solvent was then evaporated under vacuum and the dark brown re-

sidue chromatographed over silica gel. From the first yellow fraction (*n*-pentane) the 1,3,5-triphosphabenzenes **7d,e** were isolated as yellow oily residues. The second yellow band (*n*-pentane/ether, 20:1) was collected and evaporated under vacuum to yield **6c**, **6d**, or **6e** as yellow, viscous oils. The products **6d** and **6e** were further purified by crystallization from *n*-pentane at −78 °C.

3-tert-Butyl-5,7-bis(1,1-dimethylpropyl)-3-aza-1,2,4,6-tetraphosphatetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**6c**)

Yellow, viscous oil (0.19 g, 53%).

$^{31}P\{^1H\}$ NMR (C_6D_6): −123.2, −9.2 [AA′XX′ spin system, $J_{P,P}$(AX, A′X′) = 162.3, $J_{P,P}$(AA′) = 24.3, $J_{P,P}$(XX′) = 6.2, $J_{P,P}$(A′X, AX′) = 1.4 Hz]. ^1H NMR (C_6D_6): 0.85 (s, 6H), 0.88 (t, $J_{H,H}$ = 7.5 Hz, 6H), 1.18 (s, 6H), 1.52 (m_c, 4H), 1.61 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 9.1 (s), 26.8 (m_c), 28.6 (m_c), 28.7–31.3 (m), 34.2 (t, $J_{C,P}$ = 10.4 Hz), 34.7 (m_c), 35.2 (m_c), 56.6 (t, $J_{C,P}$ = 13.6 Hz). MS (EI, 70 eV): *m/z* (%) = 361 (72) [M^+], 57 (100).

3-tert-Butyl-5,7-bis(1-methylyclopentyl)-3-aza-1,2,4,6-tetraphosphatetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**6d**)

Pale yellow crystals (0.22 g, 57%); m.p. 73 °C.

$^{31}P\{^1H\}$ NMR (C_6D_6): −123.8, −5.8 [AA′XX′ spin system, $J_{P,P}$(AX, A′X′) = 161.0, $J_{P,P}$(AA′) = 23.5, $J_{P,P}$(XX′) = 5.5, $J_{P,P}$(A′X, AX′) = 1.3 Hz]. ^1H NMR (C_6D_6): 1.02 (s, 6H), 1.10–2.10 (m, 16H), 1.60 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 24.5 (s), 25.4 (m_c), 28.8–31.4 (m), 34.1 (t, $J_{C,P}$ = 10.4 Hz), 39.3 (m_c), 42.1 (m_c), 43.5 (m_c), 56.8 (t, $J_{C,P}$ = 13.6 Hz). MS (EI, 70 eV): *m/z* (%) = 385 (76) [M^+], 259 (100). – $C_{18}N_{31}NP_4$ (385.34): calcd. C 56.10, H 8.11, N 3.63; found C 56.8, H 8.5, N 3.5.

3-tert-Butyl-5,7-bis(1-methylcyclohexyl)-3-aza-1,2,4,6-tetraphosphatetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**6e**)

Pale yellow crystals (0.19 g, 47%); m.p. 76 °C.

$^{31}P\{^1H\}$ NMR (C_6D_6): −125.3, −11.9 [AA′XX′ spin system, $J_{P,P}$(AX, A′X′) = 160.9, $J_{P,P}$(AA′) = 23.3, $J_{P,P}$(XX′) = 5.6, $J_{P,P}$(A′X, AX′) = 1.3 Hz]. ^1H NMR (C_6D_6): 1.05–2.02 (m, 20H), 1.33 (s, 6H), 1.68 (s, 9H). $^{13}C\{^1H\}$NMR (C_6D_6): 22.2 (d, $J_{C,P}$ = 13.6 Hz), 23.6 (s), 26.0 (d, $J_{C,P}$ = 5.6 Hz), 28.6–30.6 (m), 31.0 (s), 33.7 (t, $J_{C,P}$ = 10.4 Hz), 34.5 (m_c), 38.6 (m_c), 39.8 (s), 56.4 (t, $J_{C,P}$ = 13.6 Hz). MS (EI, 70 eV): *m/z* (%) = 413 (34) [M^+], 57 (100). – $C_{20}H_{35}NP_4$ (413.39): calcd. C 58.11, H 8.53, N 3.39; found C 57.0, H 8.4, N 3.1.

3-(1-Adamantyl)-5,7-di-tert-butyl-3-aza-1,2,4,6-tetraphosphatetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**6f**)

To a stirred suspension of **5b** (0.32 g, 1.00 mmol) in 5 ml of toluene was added **4a** (0.40 g, 4.00 mmol) at −78 °C. Subsequently the reaction mixture was allowed to warm to 25 °C and stirred for 12 h. After removal of the solvent under vacuum, the residue was chromatographed over alumina. The first yellow fraction (*n*-pentane) was collected and evaporated under vacuum. The yellow residue was crystallized from *n*-pentane at −78 °C to yield yellow crystals (0.14 g, 34%).

$^{31}P\{^1H\}$ NMR (C_6D_6): −124.8, −13.5 [AA′XX′ spin system, $J_{P,P}$(AX, A′X′) = 161.0, $J_{P,P}$(AA′) = 21.5, $J_{P,P}$(XX′) = 5.8, $J_{P,P}$(A′X, AX′) = 1.9 Hz]. ^1H NMR (C_6D_6): 1.12 (d, $J_{H,P}$ = 1.2 Hz, 18H), 1.54 (m_c, 6H), 1.99 (m_c, 3H), 2.38 (m_c, 6H). – $^{13}C\{^1H\}$ NMR (C_6D_6): 29.8–31.7 (m), 29.9 (m_c), 30.7 (s), 32.3 (m_c), 36.0 (s), 47.8 (t, $J_{C,P}$ = 10.9 Hz), 57.1 (t, $J_{C,P}$ = 12.9 Hz). MS (EI, 70 eV): *m/z* (%) = 411 (28) [M^+], 135 (100).

1-η-[3,5,7-Tri-tert-butyl-3-aza-1,2,4,6-tetraphosphatetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane]-[tetracarbonyliron(0)] (**17**)

A suspension of **6a** (0.40 g, 1.20 mmol) and diiron nonacarbonyl (0.44 g, 1.20 mmol) in 5 ml of toluene was stirred at 25 °C for 24 h. After removal of the solvent under vacuum, the residue was taken up in 5 ml of *n*-pentane and filtered through a D3 glass sinter filled to a depth of 3 cm with Celite. After two washings with *n*-pentane (5 ml each), the combined filtrates were evaporated to dryness. The resultant solid was chromatographed over alumina. The first yellow fraction (*n*-pentane) was collected and evaporated under vacuum to furnish a mixture of **17** and unchanged **6a**. Repeated crystallizations from *n*-pentane at −78 °C afforded yellow crystals of pure **17** (0.24 g, 40%).

$^{31}P\{^1H\}$ NMR (C_6D_6): −127.2 (dd, $J_{P,P}$ = 168.7, 7.4 Hz), −40.7 (dpt, $J_{P,P}$ = 179.1, 7.0 Hz), −9.1 (dd, $J_{P,P}$ = 179.1, 23.2 Hz), 20.1 (ddd, $J_{P,P}$ = 168.7, 23.2, 6.6 Hz). ^1H NMR (C_6D_6): 1.02 (s, 9H), 1.04 (s, 9H), 1.44 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 30.1 (m_c), 30.7 (m_c), 33.0 (m_c), 34.0 (pt, $J_{C,P} \cong$ 10.0 Hz), 57.3 (pt, $J_{C,P} \cong$ 14.0 Hz), 217.3 (dd, $J_{C,P}$ = 12.1, 2.3 Hz). IR (*n*-pentane): ν = 2060 (C=O), 1982 (C=O), 1965 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 501

(<1) [M^+], 389 (100). – $C_{18}H_{27}FeNO_4P_4$ (501.16): calcd. C 43.14, H 5.43, N 2.80; found C 43.2, H 5.4, N 2.7.

1-η-[3,5,7-Tri-tert-butyl-3-aza-1,2,4,6-tetraphosphatetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane]-[pentacarbonyltungsten] (**18**)

A solution of tungsten hexacarbonyl (0.12 g, 0.34 mmol) in 60 ml of THF was placed in a photolysis apparatus and irradiated under cooling with water for 25 min using a medium-pressure mercury lamp, which resulted in the formation of the tungsten pentacarbonyl-THF complex. During this time the color of the reaction mixture changed from colorless to yellow. Then a solution of **6a** (0.10 g, 0.30 mmol) in 5 ml of THF was added and the mixture stirred for 24 h. The solvent was evaporated under vacuum and the yellow residue was subjected to column chromatography on silica gel. The first yellow fraction (*n*-pentane) was collected and evaporated under vacuum to furnish a mixture of **18** and traces of unchanged **6a**. Repeated crystallizations from *n*-pentane at –78 °C afforded yellow crystals of pure **18** (0.12 g, 61%).

$^{31}P\{^1H\}$ NMR (C_6D_6): –130.9 (dd, $J_{P,P}$ = 172.2, 6.0 Hz), –104.1 (dpt, $J_{P,P}$ = 151.7, 6.0 Hz), 1.9 (dd, $J_{P,P}$ = 151.7, 21.4 Hz), 12.3 (ddd, $J_{P,P}$ = 172.2, 21.4, 6.0 Hz). ^1H NMR (C_6D_6): 1.04 (s, 9H), 1.05 (s, 9H), 1.44 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 30.3 (m_c), 32.7 (m_c), 33.9 (pt, $J_{C,P} \cong$ 10.0 Hz), 36.5 (m_c), 38.3 (m_c), 57.5 (pt, $J_{C,P} \cong$ 14.0 Hz), 196.8 (dd, $J_{C,P}$ = 6.3, 2.7, $J_{C,W}$ = 126.8 Hz), 197.8 (d, $J_{C,P}$ = 31.4, $J_{C,W}$ = 150.8 Hz). IR (*n*-pentane): ν = 2074 (C=O), 1949 (C=O), 1919 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 657 (6) [M^+], 177 (100). – $C_{19}H_{27}NO_5P_4W$ (657.17): cald. C 34.73, H 4.14, N 2.13; found C 34.7, H 4.2, N 2.1.

μ-1:6-η:η-[3,5,7-Tri-tert-butyl-3-aza-1,2,4,6-tetraphosphatetracyclo[3.2.0.0^{2,7}.0^{4,6}]-heptane]-bis[tetracarbonyliron(0)] (**19**)

A suspension of **6a** (0.15 g, 0.45 mmol) and diiron nonacarbonyl (0.33 g, 0.90 mmol) in 5 ml of toluene was stirred at 25 °C for 24 h. After removal of the solvent under vacuum, the residue was taken up in 5 ml of *n*-pentane and filtered through a D3 glass sinter filled to a depth of 3 cm with alumina. After two washings with *n*-pentane (5 ml each), the combined filtrates were evaporated to dryness. The resultant yellow solid was purified by crystallization from *n*-pentane at –78 °C providing yellow crystals of pure **19** (0.07 g, 24%).

$^{31}P\{^1H\}$ NMR (C_6D_6): –43.9 (d, $J_{P,P}$ = 191.8 Hz), 19.6 (d, $J_{P,P}$ = 191.8 Hz). ^1H NMR (C_6D_6): 1.12 (s, 18H), 1.37 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 30.5 (m_c), 34.0 (m_c), 34.0 (t, $J_{C,P} \cong$ 10.0 Hz), 44.5 (m_c), 58.0 (t, $J_{C,P} \cong$ 14.0 Hz), 216.8 (d, $J_{C,P}$ = 11.2 Hz). IR (*n*-pentane): ν = 2068 (C=O), 2059 (C=O), 1989 (C=O), 1983 (C=O), 1970 (C=O) cm^{-1}. – MS (EI, 70 eV): *m/z* (%) = 669 (<1) [M^+], 57 (100). $C_{22}H_{27}Fe_2NO_8P_4$ (669.04): calcd. C 39.49, H 4.07, N 2.09; found C 39.8, H 3.9, N 2.0.

μ-1:6-η:η-[3,5,7-Tri-tert-butyl-3-aza-1,2,4,6-tetraphosphatetracyclo[3.2.0.0^{2,7}.0^{4,6}]-heptane]-bis[pentacarbonyltungsten] (**20**)

A solution of tungsten hexacarbonyl (0.40 g, 1.13 mmol) in 60 ml of THF was placed in a photolysis apparatus and irradiated under cooling with water for 25 min using a medium-pressure mercury lamp, which resulted in the formation of the tungsten pentacarbonyl-THF complex. During this time the color of the reaction mixture changed from colorless to yellow. Then a solution of **6a** (0.15 g, 0.45 mmol) in 5 ml THF was added and the mixture stirred for 24 h. The solvent was evaporated under vacuum and the yellow residue was placed in a sublimation apparatus to remove unchanged tungsten hexacarbonyl. After 2 h at 40 °C/10^{-2} mbar the tungsten hexacarbonyl was completely removed, the residue was taken up in 5 ml of diethylether and filtered through a D3 glass sinter filled to a depth of 3 cm with silica gel. After two washings with ether (5 ml each), the combined filtrates were evaporated to dryness. The yellow residue was purified by crystallization from *n*-pentane at –78 °C providing pure **20** as a yellow solid (0.21 g, 47%).

$^{31}P\{^1H\}$ NMR (C_6D_6): –111.9 (d, $J_{P,P}$ = 159.8, $J_{P,W}$ = 228.0 Hz), 21.7 (d, $J_{P,P}$ = 159.8 Hz). ^1H NMR (C_6D_6): 1.28 (s, 9H), 1.29 (s, 9H), 1.76 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6): 31.0 (m_c), 33.3 (m_c), 34.3 (t, $J_{C,P} \cong$ 10.2 Hz), 41.9 (m_c), 58.6 (t, $J_{C,P} \cong$ 14.0 Hz), 196.0 (m_c), 196.8 (d, $J_{C,P}$ = 33.9 Hz). IR (*n*-pentane): ν = 2073 (C=O), 1983 (C=O), 1957 (C=O), 1949 (C=O) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 981 (10) [M^+], 517 (100). $C_{24}H_{27}NO_{10}P_4W_2$ (981.07): calcd. C 29.38, H 2.77, N 1.43; found C 28.8, H 2.8, N 1.5.

General procedure for the preparation of the Staudinger products **22a-c**

A solution of **6a** (0.15 g, 0.45 mmol) and the azides **21a**, **21b,** or **21c** (0.45 mmol) in 4 ml of dichloromethane was stirred for 48 h. The solvent was evaporated under vacuum and the colorless to

pale yellow residue was washed 3 times with cold (3 °C) *n*-pentane (2 ml each). Crystallization from dichloromethane at −78 °C afforded pure **22a**,**b**,**c** as colorless solids.

3,5,7-Tri-tert-butyl-1-(4-methylsulfonylimino)-3-aza-1,2,4,6-tetraphosphatetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**22a**)

Colorless powder (0.15 g, 78%); m.p. 120 °C (decomp.).

$^{31}P\{^1H\}$ NMR (C_6D_6): −144.6 (ddd, $J_{P,P}$ = 175.4, 31.1, 14.5 Hz), −21.0 (ddd, $J_{P,P}$ = 175.4, 20.5, 9.7 Hz), 132.1 (ddd, $J_{P,P}$ = 31.1, 9.7, 4.5 Hz), 199.9 (ddd, $J_{P,P}$ = 20.5, 14.5, 4.5 Hz). – ^1H NMR (C_6D_6): 0.97 (s, 9H), 1.17 (s, 9H), 1.50 (d, $J_{H,P}$ = 1.4 Hz, 9H), 2.38 (s, 3H). – $^{13}C\{^1H\}$ NMR (C_6D_6): 28.8 (dpt, $J_{C,P}$ = 10.0, 7.2 Hz), 29.0 (dd, $J_{C,P}$ = 9.2, 8.0 Hz), 32.5 (pt, $J_{C,P}$ = 11.0 Hz), 32.8–33.3 (m), 34.1–34.5 (m), 41.6 (s), 46.7–47.9 (m), 59.3 (pt, $J_{C,P}$ = 18.3 Hz). – MS (EI, 70 eV): *m/z* (%) = 426 (12) [M$^+$], 177 (100).

3,5,7-Tri-tert-butyl-1-tosylimino-3-aza-1,2,4,6-tetraphosphatetracyclo[3.2.0.0^{2,7}.0^{4,6}]-heptane (**22b**)

Colorless powder (0.19 g, 83%); m.p. 128 °C (decomp.).

$^{31}P\{^1H\}$ NMR (C_6D_6): −146.7 (ddd, $J_{P,P}$ = 175.0, 30.6, 14.1 Hz), −22.2 (ddd, $J_{P,P}$ = 175.0, 20.5, 10.5 Hz), 130.8 (ddd, $J_{P,P}$ = 30.6, 10.5, 5.9 Hz), 198.6 (ddd, $J_{P,P}$ = 20.5, 14.1, 5.9 Hz). – ^1H NMR (CD_2Cl_2): 1.18 (s, 9H), 1.26 (s, 9H), 1.82 (d, $J_{H,P}$ = 1.2 Hz, 9H), 2.60 (s, 3H), 7.50 (d, $J_{H,H}$ = 8.8 Hz, 2H), 7.88 (d, $J_{H,H}$ = 8.8 Hz, 2H). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 20.7 (s), 27.7 (dd, $J_{C,P}$ = 17.0, 6.8 Hz), 28.0 (pt, $J_{C,P}$ = 8.7 Hz), 31.8 (pt, $J_{C,P}$ = 11.0 Hz), 32.4 (m$_c$), 33.4 (m$_c$), 43.5 (m$_c$), 47.6 (m$_c$), 58.5 (pt, $J_{C,P}$ = 18.2 Hz), 125.8 (s), 128.9 (s), 138.3 (s), 142.6 (s). – MS (EI, 70 eV): *m/z* (%) = 502 (17) [M$^+$], 91 (100). $C_{21}H_{34}N_2O_2P_4S$ (502.46): calcd. C 50.20, H 6.82, N 5.58; found C 49.1, H 6.7, N 5.9.

3,5,7-Tri-tert-butyl-1-[(4-acetamido)phenylsulfonylimino]-3-aza-1,2,4,6-tetraphosphatetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**22c**)

Colorless powder (0.19 g, 78%); m.p. 134 °C (decomp.).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): −142.7 (ddd, $J_{P,P}$ = 175.2, 31.5, 13.8 Hz), −19.6 (ddd, $J_{P,P}$ = 175.2, 19.7, 9.0 Hz), 133.9 (ddd, $J_{P,P}$ = 31.5, 9.0, 6.1 Hz), 203.2 (ddd, $J_{P,P}$ = 19.7, 13.8, 6.1 Hz). ^1H NMR (CD_2Cl_2): 0.93 (s, 9H), 1.03 (s, 9H), 1.57 (s, 9H), 2.11 (s, 3H), 7.68 (s, 4H), 8.39 (s, 1H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 15.6 (s), 24.0 (s), 26.2 (s), 34.1 (pt, $J_{C,P}$ = 11.4 Hz), 34.7 (m$_c$), 35.7 (m$_c$), 45.7 (m$_c$), 50.1 (m$_c$), 60.9 (pt, $J_{C,P}$ = 17.8 Hz), 120.7 (s), 129.2 (s), 137.6 (s), 144.2 (s), 170.8 (s). IR (CCl_4): ν = 1708 cm^{-1} (C=O). MS (EI, 70 eV): *m/z* (%) = 545 (10) [M$^+$], 177 (100).

3,5,7-Tri-tert-butyl-1,2-ditosylimino-3-aza-1,2,4,6-tetraphosphatetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane (**23**)

A solution of **6a** (0.20 g, 0.60 mmol) and tosyl azide (**21b**) (0.24 g, 1.20 mmol) in 5 ml of dichloromethane was stirred for 3 d. The solvent was evaporated under vacuum and the colorless to pale yellow residue was washed 3 times with *n*-pentane (2 ml each). Crystallization from dichloromethane at −78 °C afforded pure **23** as a pale yellow powder (0.30 g, 74%); m.p. 110 °C (decomp.).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): −147.4 (dpt, $J_{P,P}$ = 172.9, 13.6 Hz), 15.0 (pt, $J_{P,P}$ = 13.6 Hz), 26.2 (dd, $J_{P,P}$ = 172.9, 23.7 Hz), 155.5 (dpt, $J_{P,P}$ = 23.7, 13.6 Hz). ^1H NMR (CD_2Cl_2): 1.11 (s, 9H), 1.32 (s, 9H), 1.63 (s, 9H), 2.38 (s, 6H), 7.25 (d, $J_{H,H}$ = 7.8 Hz, 2H), 7.27 (d, $J_{H,H}$ = 8.3 Hz, 2H), 7.84 (d, $J_{H,H}$ = 8.3 Hz, 2H), 7.94 (d, $J_{H,H}$ = 7.8 Hz, 2H). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 23.5 (s), 23.7 (s), 31.9 (pt, $J_{C,P}$ = 10.2 Hz), 32.6 (dd, $J_{C,P}$ = 15.2, 8.5 Hz), 33.9 (m$_c$), 35.2 (pt, $J_{C,P}$ = 10.6 Hz), 36.6 (m$_c$), 37.4 (m$_c$), 61.9 (pt, $J_{C,P}$ = 17.8 Hz), 128.3 (s), 128.6 (s), 131.2 (s), 131.8 (s), 144.0 (s), 144.6 (s), 145.2 (s), 146.9 (s). – MS (EI, 70 eV): *m/z* (%) = 671 (6) [M$^+$], 91 (100).

2,4,6-Tri-tert-butyl-3,5-dichloro-2-aza-1,3,5,7-tetraphosphatricyclo[2.2.1.0^{6,7}]heptane (**24**)

To a stirred solution of **15a** (0.08 g, 0.34 mmol) in 5 ml toluene was added dropwise a solution of **6a** (0.11 g, 0.34 mmol) in 5 ml of toluene at 25 °C and the mixture stirred for 7 d. After removal of the solvent under vacuum, the residue was taken up in a mixture of 5 ml of *n*-pentane and 5 ml of toluene and then filtered through a D4 glass sinter. The filtrate was concentrated to 10% of its volume. Cooling to −78 °C and filtration furnished **24** as a colorless powder (0.02 g, 18%).

$^{31}P\{^1H\}$ NMR (C_6D_6): −112.3 (ddd, $J_{P,P}$ = 207.5, 44.8, 12.2 Hz), −9.1 (ddd, $J_{P,P}$ = 207.5, 20.4, 8.1 Hz), 93.9 (dd, $J_{P,P}$ = 44.8, 8.1 Hz), 225.5 (dd, $J_{P,P}$ = 20.4, 12.2 Hz). ^1H NMR (C_6D_6): 1.03 (pt, $J_{H,P}$ = 1.3 Hz, 9H), 1.32 (d, $J_{H,P}$ = 1.5 Hz, 9H), 1.54 (d, $J_{H,P}$ = 2.2 Hz, 9H). – MS (EI, 70 eV): *m/z* (%) = 403 (44) [M$^+$], 266 (100).

1,3,4-Tri-tert-butyl-1,2,5-azadiphosphole (**11a**)

Phosphaalkyne **4a** (0.11 g, 1.10 mmol) at −78 °C was added to a stirred solution of **5a** (0.17 g,

0.53 mmol) in 12 ml of toluene. The mixture was allowed to warm up, and stirred for 30 min at room temperature, and then the solvent was evaporated under vacuum. After extraction with *n*-pentane (20 ml), the solvent was distilled off under reduced pressure, and the residue purified by bulb-to-bulb distillation (140 °C/10^{-2} mbar) yielding an inseparable mixture of quadricyclane **6a** and 1,2,5-azadiphosphole **11a**.

$^{31}P\{^1H\}$ NMR (C_6D_6): 285.8 (s). – ^1H NMR (C_6D_6): 1.59 (t, $^4J_{H,P}$ = 0.9 Hz, 9H), 1.66 (d, $^4J_{H,P}$ = 3.0 Hz, 18H). – $^{13}C\{^1H\}$ NMR (C_6D_6): 34.9 (t, $^3J_{C,P}$ = 9.3 Hz, NC**Me**$_3$), 35.3 (d, $^3J_{C,P}$ = 19.5 Hz, CC**Me**$_3$), 37.6 (dd, $^2J_{C,P}$ = 27.2 Hz, $^3J_{C,P}$ = 1.7 Hz, C**C**Me$_3$), 59,4(t, $^2J_{C,P}$ = 12,7 Hz, N**C**Me$_3$), 180.7 (dd, $^1J_{C,P}$ = 47.5 Hz, $^2J_{C,P}$ = 11.4 Hz, **C**CMe$_3$). (NMR data were determined from a mixture of **6a**/**11a**; the signals of pure **6a** are known).

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