Organophosphorus Compounds; 129.[1] Mesitylphosphaacetylene: Synthesis and Reactivity Studies of a New Phosphaalkyne

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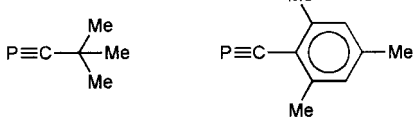
Abstract: Mesitylphosphaacetylene **(1b)** has been synthesized by $AlCl_3$ initiated elimination of bis(trimethylsilyl) ether from the phosphaalkene **2b**. This new phosphaalkyne undergoes [3+2] cycloaddition reactions with diazo compounds (→ **6a**,**b**), azides (→ **8a–c**), and nitrile oxides (→ **10a**,**b**) to yield five-membered heterocyclic products. The mesoionic reaction partners **11** and **13** react with **1b** under elimination of CO_2 and COS, respectively, to furnish the 1,3-aza- and 1,3-thiaphospholes **12** and **14**. Reaction of **1b** with buta-1,3-diene leads to the diphosphatricyclooctene **18**; it has been shown that the 1-phosphacyclohexa-1,4-diene **15** (characterized by an X-ray structure analysis of its $W(CO)_5$ complex **17**) is an intermediate in the multistep reaction. Moreover, **1b** has been characterized by Diels–Alder reactions with the cyclobutadiene **19** and the azacyclobutadiene **21** to afford the Dewar hetarenes **20** and **22**.

Key words: mesitylphosphaacetylene, heterophospholes, [3+2] cycloaddition reactions, Diels–Alder reactions, Dewar hetarenes

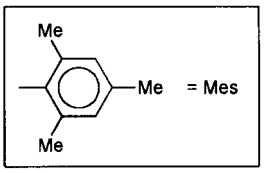
Introduction

tert-Butylphosphaacetylene **(1a)** has played a dominating role in investigations on the chemistry of kinetically stabilized phosphaalkynes. Its reactivity has been investigated more thoroughly than that of any other compound with a P/C triple bond.[2–5] In general, phosphaalkynes bearing tertiary alkyl substituents have an unusually high thermal stability whereas the steric shielding of the bulky group in **1a** has only a limited influence on the reactivity.



1a

1b



In marked contrast to alkyl-substituted phosphaalkynes, our knowledge about phosphaalkynes bearing aryl substituents is sparse: the rather unstable phenylphosphaacetylene[6] is not accessible in the amounts needed for reactivity studies and, although 2,4,6-tri-*tert*-butylphenylphosphaacetylene is more easily prepared, the reactivity of its P/C triple bond is markedly reduced by the extreme shielding of the supermesityl group.[7] In this context mesitylphosphaacetylene **(1b)** occupies an intermediate position and thus we were prompted to investigate the synthetic potential of this aryl-substituted phosphaalkyne.

In general, β-elimination reactions of suitably substituted phosphaalkenes **2a,b** have proved to be valuable for the synthesis of kinetically substituted phosphaalkynes. In particular, optimized elimination conditions for P/C triple bond systems bearing tertiary alkyl groups consist of the NaOH catalyzed elimination of hexamethyldisiloxane at 110–150 °C in the absence of a solvent.[8] This strategy was also applied to the preparation of mesitylphosphaalkyne.[8] However, we were not able to reproduce the reported synthesis with a yield of 43%. Since **1b** cannot be removed rapidly enough from the reaction vessel due to its relatively high boiling point of 50 °C/10^{-3} mbar, the required reaction temperature (150 °C) always leads to a high percentage of polymerization products of **1b**.

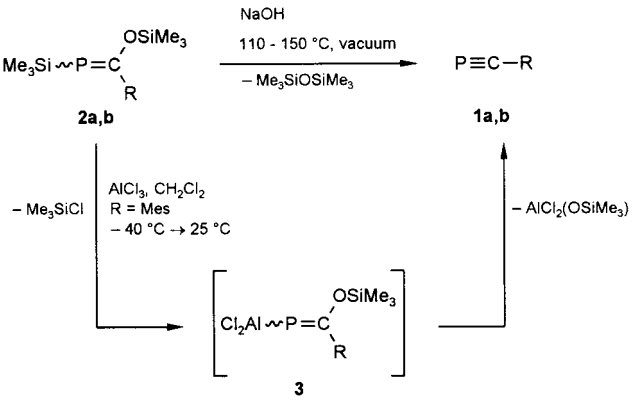
For this reason we sought an easier, alternative process which avoids high temperatures. In 1996 Breit et al. reported[9] an efficient and quantitative synthesis of *tert*-butylphosphaacetylene **(1a)** by elimination of hexamethyldisiloxane from **2a** in the presence of a stoichiometric amount of aluminum trichloride at comparably low temperatures. However, in this case the phosphaalkyne could not be separated from concomitantly formed chlorotrimethylsilane and the dichloromethane used as solvent. From a mechanistic point of view, the initial step of this procedure probably comprises the formation of the alanylphosphaalkene **3**. Final elimination of $AlCl_2(OSiMe_3)$ furnishes the phosphaacetylene **1a**. Hence we have now investigated the reactivity of the mesitylphosphaalkene **2b** towards aluminum trichloride.

Synthesis of Mesitylphosphaacetylene (1b): Synthesis of the *E*/*Z*-Mesitylphosphaalkene 2b

The phosphaalkene **2b** is easily prepared by reaction of lithium bis(trimethylsilyl)phosphide·2THF[10] with mesitylene-2-carboxylic acid chloride[11] at –40 °C. After the initial elimination of lithium chloride the (not detectable) acylphosphane undergoes spontaneous rearrangement to an *E*/*Z*-isomeric mixture of phosphaalkene **2b**, which can be isolated in good yields by bulb-to-bulb distillation. The pure *E*-isomer is obtained by crystallization from pentane. However, in solution rapid (<15 min) isomerization occurs and the *E*/*Z* mixture is obtained again. *E*/*Z*-Mesitylphosphaalkene **2b** was fully characterized by analytical and spectroscopic data which are typical for phosphaalkenes[12] and accordingly are not discussed further.

Synthesis of Mesitylphosphaacetylene (1b): Reaction of 2b with Aluminum Trichloride

When a solution of **2b** in dichloromethane is added dropwise to a suspension of aluminum trichloride/dichloromethane at –40 °C, low temperature ^{31}P NMR monitoring of the reaction reveals the quantitative formation of mesitylphosphaacetylene **(1b)**. Workup by rapid distillation and subsequent filtration over silica gel with pentane leads to the pure product **1b** isolated in a yield of 30%. In contrast to the thermal (NaOH catalyzed) process (with a higher, but not reproducible yield of 43%), the described aluminum trichloride initiated procedure is absolutely reliable.



1 - 3	a	b
R	*t*-Bu	Mes

At room temperature, mesitylphosphaacetylene **(1b)** is a colorless viscous oil which crystallizes at ca. –5 to –10 °C and is best stored as such at –78 °C because it decomposes slowly but noticeably at about 25 °C. Having this reliable and reproducible synthetic method at hand, detailed reactivity studies of **1b** became possible.

As previously mentioned, *tert*-butylphosphaacetylene **(1a)** has been used mainly as the model substrate for studies on the reactivity of phosphaalkynes.[8] Compound **1a** shows a very pronounced tendency to undergo cycloaddition,[2–5] ene,[13] and cyclooligomerization[5, 14] reactions. In this paper we concentrate mainly on novel 1,3-dipolar and [4+2] cycloaddition reactions of mesitylphosphaacetylene **(1b)**.

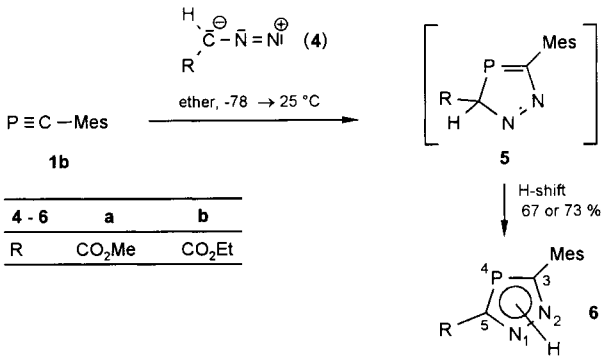
[3+2] Cycloaddition Reactions with Diazo Compounds, Azides, and Nitrile Oxides

Phospholes containing further heteroatoms in the ring play a significant role in the development of the chemistry of low-coordinated phosphorus.[2–4] Since phosphaalkynes possess a cycloaddition potential similar to that of alkynes and since a large selection of 1,3-dipoles is available, the range of accessible phospholes has been greatly expanded by various [3+2] cycloaddition reactions.[2–4] The [3+2] cycloaddition potential of the model substrate *tert*-butylphosphaacetylene toward numerous diazo compounds has been investigated most thoroughly[15, 16] and so we have now studied analogous reactions with mesitylphosphaacetylene **(1b)**.

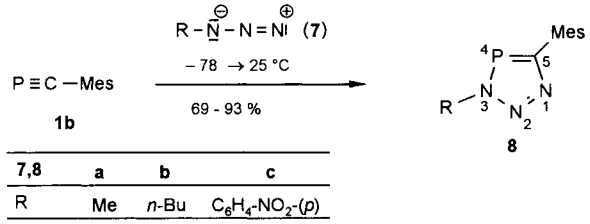
The use of α-diazoalkanes **4a,b** gives rise to the selective formation of the 1,2,4-diazaphospholes **6a,b**, which are isolated in good yields by column chromatography. The primary products of the reaction are the 3*H*-1,2,4-diazaphospholes of which **5b** has been detected at –50 °C by NMR spectroscopy in the example of the cycloaddition of mesitylphosphaacetylene **(1b)** with the diazo compound **4b**. Thus, **5b** exhibits a ^{31}P NMR signal at remarkably low field (δ = 297.6) compared to the tert-butyl derivative (δ = 223.7). The sigmatropic [1,5]-proton shifts to furnish **6** are observed at 0 °C and are facilitated by the gain in aromatization energy.

In analogy to the reaction of **4a,b** with alkyl-substituted phosphaalkynes no 1,2,3-diazaphosphole is formed. Ab initio calculations on the parent compounds show that the observed regioselectivity results from the energy difference of the transition states. The barrier calculated for the initial formation of 3*H*-1,2,4-diazaphosphole is lower than that for 1,2,3-diazaphosphole. The [3+2] cycloaddition is therefore under kinetic control.[17]

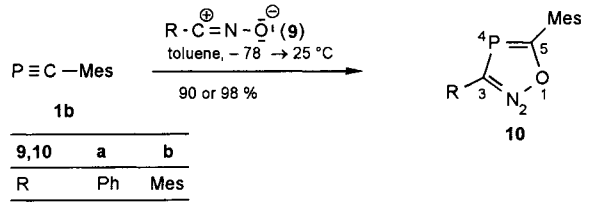
Similar to the intermediates **5**, the mesityl-substituted 1,2,4-diazaphospholes **6** show low field shifts in their ^{31}P NMR spectra ($\Delta\delta$ = +8.1 for **5a**) compared to the *tert*-but-



4 - 6	a	b
R	CO_2Me	CO_2Et



7,8	a	b	c
R	Me	*n*-Bu	C_6H_4-NO_2-(*p*)



9,10	a	b
R	Ph	Mes

yl-substituted rings[15,16] (Table). This is most likely caused by the negative inductive effect of the mesityl group as opposed to the positive inductive effect of the *tert*-butyl group. In the ^{13}C NMR spectra both ring carbon atoms (C3, C5) are detected as doublet signals with characteristic $^1J(C,P)$ coupling constants at δ = 167.9 [$^1J(C,P)$ = 61.0 Hz] and 175.3 [$^1J(C,P)$ = 53.8 Hz]. The NH absorption in the IR (ν = 3165 cm^{-1}) and the signals in the ^1H NMR spectra (δ = 11.36 for **6a**) clearly indicate that the nitrogen is bonded to the original diazomethyl hydrogen atom.

1,2,3,4-Triazaphospholes are easily accessible by reaction of alkyl-substituted phosphaalkynes.[15] Starting from **1b** regiospecific [3+2] cycloadditions with azides **7a–c** take place to furnish the mesityl-substituted 1,2,3,4-triazaphospholes **8a–c** in good to high yields. The regiochemistry is easily deduced from the significant $^3J(H,P)$ coupling constant of 6.6 Hz for the methyl protons in **8a**. Although the ^{31}P NMR signals are in the range typical for 1,2,3,4-triazaphospholes[15] comparison with the *tert*-butyl derivative again reveals a low-field shift of $\Delta\delta$ = +9.0 (for **8a**) (Table). Interestingly, the ^{13}C NMR signal of the mesityl-substituted ring carbon C5 is observed at δ = 181.0, a noticeably upfield shift (δ = 198.3 for *tert*-butyl substitution).

The well known 1,3-dipolar cycloadditions of *tert*-butylphosphaacetylene with nitrile oxides[18] can also be transferred to the novel phosphaalkyne **1b**. Benzonitrile oxide **(9a)** and mesitylene-2-carbonitrile oxide **(9b)** undergo rapid addition to furnish the 3,5-diaryl-1,2,4-oxazaphospholes **10a,b**, isolated in high yields by bulb-to-bulb distillation or crystallization. The dipole orientation is such as to provide an optimal separation between the sterically demanding substituents and is the same as that for **1a**.[18] Although thermodynamically more favored, the 1,2,5-oxazaphosphole ring is not formed. In accordance with the 1,2,4-diazaphospholes **6**, the 3,5-diaryl compounds **10** show significant shifts of the ^{31}P NMR signals to lower field ($\Delta\delta$ = +15.3) in comparison to those with *tert*-butyl substitution at C5. In the ^{13}C NMR spectrum of **10b** the mesityl substitution leads to a significant upfield shift of the signal for C5 (δ = 210.2) as compared to *tert*-butyl substitution (δ = 226.5). The resonance for C3, however, has the same chemical shift of δ = 180.0 (Table). Both ring carbon atom signals are typically split into doublets with characteristic $^1J(C,P)$ coupling constants of about 60 Hz.

[3+2] Cycloaddition Reactions with Mesoionic Compounds

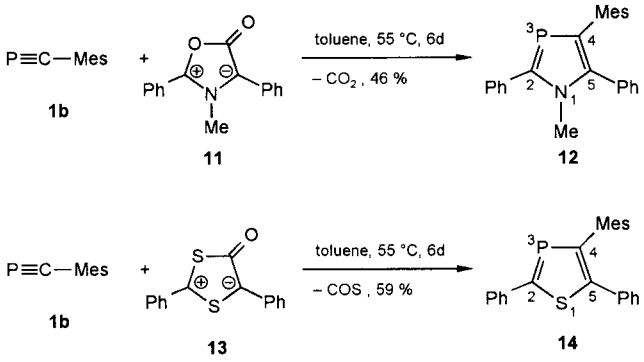
As reported for **1a**,[19] mesitylphosphaacetylene **(1b)** also undergoes smooth reactions with the mesoionic compounds **11** and **13** to furnish the 1,3-azaphosphole **12** or the 1,3-thiaphosphole **14**; the reactions proceeding at relatively low temperatures (55°C). However, the primary formed bicyclic adducts cannot be detected: spontaneous extrusion of carbon dioxide (→ **12**) or carbon oxide sul-

Table. Selected NMR Data (δ) of New Compounds Compared to the known *tert*-Butyl Derivatives

		6a		**8a**		**10b**		**12**		**14**		**20**		**22**	
R		Mes	*t*-Bu	Mes	*t*-Bu	Mes	*t*-Bu	Mes	*t*-Bu	Mes	*t*-Bu	Mes	*t*-Bu	Mes	*t*-Bu
^{31}P		105.7	97.6	182.5	173.5	92.2	76.9	106.0	96.6	217.5	220.6	335.9	314.0	230.4	202.2
^{13}C	C3	167.9[a]	164.9	181.0	198.3	180.0	179.9	170.8[a]	166.7	177.4[a]	171.2	224.0	239.8	225.9	242.2
	C5	175.3[a]	192.1			210.2	226.5	141.3[a]	156.4	157.4[a]	174.6	72.8	67.1	89.7	82.6
								142.1	140.7	150.3	149.2				

[a] exact assignment not possible.

fide (→ **14**) occurs. As expected from the results with the above discussed heterophospholes, the ^{31}P NMR signal of the 1,3-azaphosphole **12** is shifted downfield to 106.0 ppm ($\Delta\delta$ = +9.4 compared to *tert*-butyl substitution)[19] (Table).

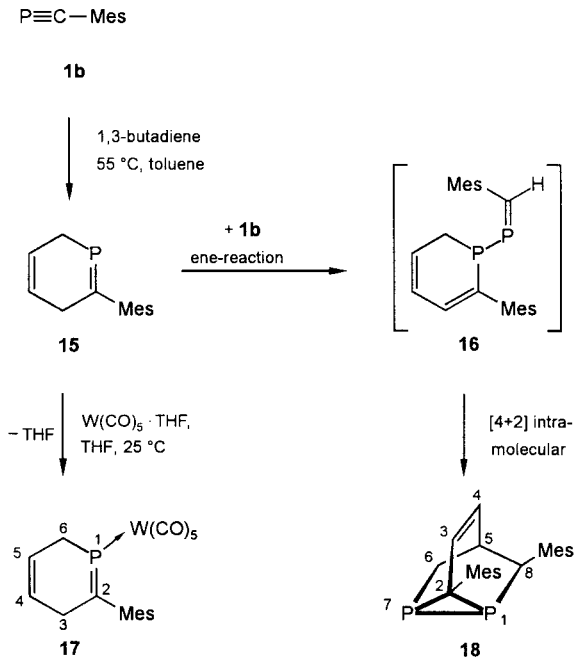


The 1,3-thiaphosphole **14** is an exception: in this case the ^{31}P NMR chemical shift of δ = 217.5 is similar to that of the product formed from **1a** (δ = 220.6). The ^{13}C NMR chemical shifts and *J*(C,P) coupling values of **12** and **14** unambiguously prove the formation of 1,3-azaphosphole and 1,3-thiaphosphole ring systems. Each ring carbon signal is split into a doublet with characteristic *J*(C,P) values. When compared to those of the *tert*-butyl derivative, the ^{13}C NMR signals for C2 (δ = 170.8) and C5 (δ = 142.1) in the nitrogen containing compound **12** are typical while that of C4 (δ = 141.3) is significantly shifted upfield ($\Delta\delta$ = –15.1).[19] In the thiaphosphole **14**, mesityl substitution at C4 results in a marked upfield shift[20] of the signal for either C2 or C4 to δ = 157.4 while the other carbon shows a typical value of δ = 177.4 (Table).

[4+2] Cycloaddition Reactions with Buta-1,3-diene

The main purpose of the studies of reactions of kinetically stabilized phosphaalkynes with 1,3-dienes was to synthesize 1-phosphacyclohexa-1,4-dienes. However, at 90 °C these reactions lead exclusively to the unexpected diphosphatricyclooctenes.[21] Their formation can be rationalized by a reaction sequence starting with an initial [4+2] cycloaddition, which is followed by a phospha-ene reaction, and a final intramolecular [4+2] cycloaddition. In the case of alkyl-substituted phosphaalkynes the primarily formed Diels–Alder adducts have not yet been detected.[22]

In contrast, the analogous reaction of mesitylphosphaacetylene **(1b)** now provides the first access to a 1-phosphacyclohexa-1,4-diene when the reaction is performed at relatively low temperatures (55 °C) in toluene as a solvent. The phosphaalkene **15** can be isolated and characterized by ^{1}H, ^{31}P NMR, and mass spectroscopy. However, complete purification of **15** is not possible due to unselective decomposition processes occurring during bulb-to-bulb distillation or column chromatography. The ^{31}P NMR signal at δ = 215.7 clearly indicates that a phosphaalkene unit is present in the product. Moreover, the 100% molecular ion peak in mass spectrum indicates that **15** is a 1:1 adduct of **1b** with buta-1,3-diene.



The stability of the Diels–Alder adduct **15** is increased significantly by coordination of one tungsten pentacarbonyl fragment at phosphorus. Complete purification of the η^1-complex **17** (63%) is possible by column chromatography on silica gel and the complete set of analytical and spectroscopic data can be obtained. The tungsten fragment at phosphorus leads to a significant upfield shift to δ = 170.0 in the ^{31}P NMR spectrum. The ^{1}J(P,W) coupling constant of 259.6 Hz is typical for W(CO)$_5$–phosphaalkene complexes.[23] On comparison with the [2-methyl-1-phosphacyclohexene]pentacarbonyltungsten complex [δ = 161.8, ^{1}J(P,W) = 246.6 Hz][22] good agreement of the ^{31}P and ^{13}C NMR data for the phosphaalkene subunits is seen. In the phosphacyclohexadiene complex **17** the sp^2-carbon C2 appears as a doublet at δ = 181.4 with a characteristic ^{1}J(C,P) splitting of 47.5 Hz. The other carbon directly bonded to phosphorus (C6) is observed at δ = 37.5 with a small ^{1}J(C,P) coupling of 9.3 Hz. The C3 signal is seen at comparable field [δ = 31.4, ^{2}J(C,P) = 2.6 Hz]. The two sp^2-carbon atoms of the C/C double bond show typical signals at δ = 120.3 and 125.4 while the equatorial and axial carbonyl carbons of the metal fragment are observed at δ = 194.5 and 198.8 with typical splitting patterns.

The constitution of **17** suggested by the NMR data has been confirmed by a crystal structure analysis (Figure), which shows a planar 1-phosphacyclohexa-1,4-diene ring: The mean deviation from the best plane is 0.005 Å; all torsion angles are in the range of –1.2 to +0.7°. The plane of the mesityl ring at C2 is perpendicular to that of the phosphacyclohexadiene ring as can be deduced from the torsion angles (C3/C2/C21/C22 –87.9°, C3/C2/C21/C26 90.4°, P1/C2/C21/C22 92.5°, P1/C2/C21/C26 –89.2°).

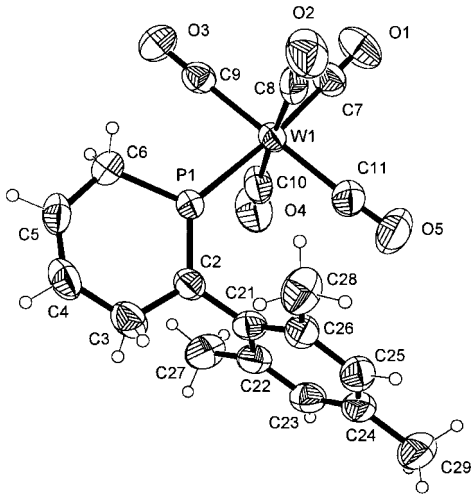


Figure. Structure of **17** in the crystal. Selected bond lengths [Å] and bond angles [°]: P1–C2 1.670 (6), P1–C6 1.826(6), P1–W1 2.467(2), C2–C3 1.504(8), C3–C4 1.483(9), C4–C5 1.321(10), C5–C6 1.484(9), C2–C21 1.481(8); C2–P1–C6 107.9(3), C2–P1–W1 132.8(2), C6–P1–W1 119.3(2), P1–C6–C5 115.3(4), P1–C2–C3 124.2(4), P1–C2–C21 119.7(4), C3–C2–C21 116.2(5), C2–C3–C4 118.2(5), C3–C4–C5 126.2(6), C4–C5–C6 128.3(6).[42]

As expected, the organophosphorus ligand **15** occupies an axial position on the tungsten pentacarbonyl fragment with a typical planar coordination geometry. The P1/C2 bond length of 1.670(6) Å is typical for η^1-complexed[24] and non-complexed[25] phosphaalkenes and clearly indicates that the coordination of $W(CO)_5$ in **17** has no significant effect on the geometry of the phosphaalkene subunit. However, the P1/W1 bond distance of 2.467(2) Å is somewhat shorter in comparison to the average values reported in the literature.[24] The C4/C5 bond length of 1.321(10) Å and the P1/C6 bond length are of normal magnitudes for C/C double and P/C single bonds.

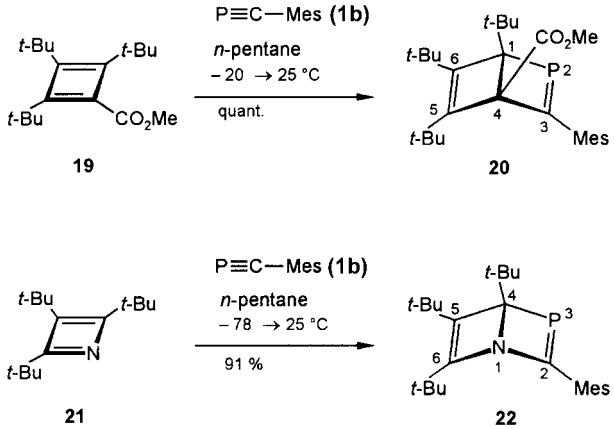
Even though the ene/[4+2] cycloaddition reaction with a further equivalent of mesitylphosphaacetylene **(1b)** is slow, it is possible to synthesize the 1,7-diphosphatricyclooctene **18**. This cage compound is characterized by mass spectrometry (*m/z* = 378) and characteristic doublet resonances in the ^{31}P NMR spectrum at δ = –168.0 and –163.1 with ^1J(P,P) couplings of 158.3 Hz. On comparison with the *tert*-butyl derivative (δ = –210.6 and –165.6)[20] it is seen that one ^{31}P NMR signal of **18** is shifted significantly downfield while the other has a comparable chemical shift of around δ = –165.

[4+2] Cycloaddition Reactions with Cyclobutadienes

Just as the reactant pair "cyclobutadiene/acetylene" opened an access to the chemistry of the valence isomers of benzene,[26] valence isomers of (hetero)phosphabenzenes are obtained by using alkyl-substituted phosphaalkynes and cyclic 1,3-dienes such as **19**[27] and **21**.[28]

Mesitylphosphaacetylene **(1b)** undergoes an analogous reaction with the kinetically stabilized cyclobutadiene-carboxylate **19** to give the 2-Dewar-phosphinine **20** regioselectively and in quantitative yield. However, purification of the bicyclic compound **20** by bulb-to-bulb distillation is not possible due to thermal decomposition at the required high temperatures.

Again the mesityl substitution leads to a marked low-field shift (δ = 335.9) in the ^{31}P NMR spectrum when compared with the *tert*-butyl derivative (δ = 314.0). In the ^{13}C NMR spectrum of **20** the former sp-carbon of **1b** (now C3) is observed at δ = 224.0, i.e., a dramatic upfield shift ($\Delta\delta$ = –15.8 *vs. tert*-butyl substitution). The same effect has been observed in the heterocyclic compounds **6**, **8**, **10**, **12**, **14**, and **22** (Table). In contrast to C3, ^{13}C NMR data of the remaining skeletal carbon atom are in good agreement with those of the *tert*-butyl derivative.



Tri-*tert*-butylazete **(21)** also reacts regioselectively with mesitylphosphaacetylene to afford the expected Dewar-1,3-azaphosphabenzene **22**, isolated in 91% yield as colorless crystals. As is the case of the Dewar-2-phosphabenzene **20**, the ^{31}P NMR signal of the 1-aza derivative **22** at δ = 230.4 shows a dramatic low field shift ($\Delta\delta$ = +28.2 compared to *tert*-butyl substitution).[28] The ^{13}C NMR resonances and J(C,P) coupling values of the skeletal carbon atoms are in good accord with those of the *tert*-butyl derivative, with the exception of C2: the phosphaalkene carbon atom is found at δ = 225.9, i.e., a remarkable upfield resonance shift ($\Delta\delta$ = –16.9) (Table).

Conclusions

This new synthesis of mesitylphosphaacetylene **(1b)** mediated by aluminum trichloride has made extensive reactivity studies possible. In the investigated [3+2] and [4+2] cycloaddition reactions **1b** shows parallels to *tert*-butylphosphaalkyne **(1a)**. However, **1b** is generally slightly less reactive so that the reactions proceed more slowly than those of **1a**. In the case of buta-1,3-diene, formation of the [4+2]-cycloadduct **1b** is faster than the subsequent ene-reaction, thus the reaction can be stopped at this stage (using one equivalent of **1b**). This led to the first synthesis and isolation of a 1-phosphacyclohexa-1,4-diene **15** and

its $W(CO)_5$ complex **17**. This example shows that the electronically altered P/C triple bond resulting from mesityl substitution may facilitate the synthesis of structurally new compounds. For this reason we will investigate the reactivity of mesitylphosphaalkyne **1b** in more detail. Investigations on thermally induced and metal-mediated cyclooligomerization reactions are underway and may provide further promising results.

All reactions were performed under argon (purity >99.998%) using Schlenk techniques. The solvents were dried by standard procedures, distilled, and stored under argon. Compounds **4a**,[29] **4b**,[30] **7a**,[31] **7b**,[32] **7c**,[33] **9b**,[34] **11**,[35] **13**,[36] **19**,[26] **21**,[37] lithium bis(trimethylsilyl)-phosphide•2 THF,[10] mesitylene-2-carboxylic acid chloride,[11] benzohydroxamic acid chloride,[38] and $W(CO)_5(THF)$[39] were prepared by the published methods. Column chromatography was performed in water-cooled glass tubes under argon. The eluate was monitored with a UV absorbance detector (λ = 254 nm). Silica gel was heated for 3 h in vacuo and then deactivated with 4% water (Brockmann activity II). The bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus, the temperatures stated are oven temperatures. Mps were determined on a Mettler FP61 apparatus (heating rate 3 °C/min) and are uncorrected. Microanalyses were performed with a Perkin–Elmer Analyser 2400. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AC 200 and Bruker AMX 400 spectrometers using TMS or solvent as internal standard. ^{31}P NMR spectra were measured on a Bruker AC 200 (80.8 MHz) spectrometer with 85% H_3PO_4 as external standard. MS were recorded with a Finnigan MAT 90 spectrometer at 70 eV. IR spectra were measured on Perkin–Elmer 16 PC FT-IR and Perkin–Elmer 1310 spectrophotometers.

(*E*,*Z*)-[Mesityl(trimethylsiloxy)methylene]trimethylsilylphosphane (2b):

Lithium bis(trimethylsilyl)phosphide•2 THF (9.85 g, 30 mmol) in pentane (150 mL) was added dropwise under magnetic stirring to a cooled solution (–40 °C) of mesitylene-2-carboxylic acid chloride (5.48 g, 30 mmol) in pentane (150 mL). LiCl precipitated in the course of the reaction. The mixture was then allowed to warm up to 25 °C and stirring was continued for 30 min. After concentration of the suspension, LiCl was removed by centrifugation. The solvent was then removed at 25 °C/10^{-3} mbar and the oily residue purified by bulb-to-bulb distillation at 150–160 °C/10^{-2} mbar to furnish a pale yellow oil which partially crystallized; yield: 7.11 g (73%) of the *E*/*Z*-isomeric mixture.

Isomer *E*-**2b** was isolated as such by crystallization from pentane; mp 77 °C.

IR (film): ν = 2950, 1605, 1370, 1250, 1205, 1175, 1000, 980, 940 cm^{-1}.

^{31}P NMR (C_6D_6): δ = 126.3 (s, *E*-**2b**, 64%), 122.4 (s, *Z*-**2b**, 36%).

^{1}H NMR (C_6D_6): *E*-**2a**: δ = 0.05 [d, ^3J(H,P) = 4.4 Hz, 9H, $PSi(CH_3)_3$], 0.47 [d, ^5J(H,P) = 1.1 Hz, 9H, $OSi(CH_3)_3$], 2.10 (s, 3H, *p*-CH_3), 2.43 (s, 6H, *o*-CH_3), 6.70 (s, 2H, aryl-H).

***Z*-2a**: δ = –0.04 [s, 9H, $OSi(CH_3)_3$], 0.50 [d, ^3J(H,P) = 3.6 Hz, 9H, $PSi(CH_3)_3$], 2.10 (s, 3H, *p*-CH_3), 2.36 (s, 6H, *o*-CH_3), 6.70 (s, 2H, aryl-H).

^{13}C NMR (C_6D_6): *E*,*Z*-**2b**: δ = 0.7–1.1 [2 $Si(CH_3)_3$ (*E*), 2 $Si(CH_3)_3$ (*Z*), due to overlap no exact assignment possible], 20.3 (s, *o*-CH_3), 21.6 (s, *p*-CH_3), 128.6 (s, *m*-C), 134.2 [d, ^3J(C,P) = 4.2 Hz, *o*-C], 137.6 (s, *p*-C), 143.4 (d, ^2J(C,P) = 9.7 Hz, *i*-C], 198.2 [d, ^1J(C,P) = 54.1 Hz, P=C(*E*)], 205.5 [d, ^1J(C,P) = 61.7 Hz, P=C(*Z*)].

$C_{16}H_{29}OPSi_2$	calcd	C	59.21	H	9.01
(324.55)	found		58.90		8.96

Mesitylphosphaacetylene (1b):

To a suspension of freshly sublimed $AlCl_3$ (822 mg, 6.16 mmol) in CH_2Cl_2 (15 mL) a solution of **2b** (2.0 g, 6.16 mmol) in CH_2Cl_2 (10 mL) was added dropwise under vigorous magnetic stirring at –40 °C. The mixture was held for 2 h at this temperature. The solvent and TMSCl were removed at –20 °C/10^{-3} mbar to leave a dark brown residue. Immediate distillation (50 – 70 °C/10^{-3} mbar) gave a colorless oil. Further purification was achieved by filtration through a D3 sinter filled with silica gel and pentane (50 mL) as eluent. The solvent was finally removed at 25 °C/10^{-3} mbar to give **1b** as a colorless oil which crystallized at around –5 °C; yield: 299 mg (30%; **1b** is best stored at –78 °C).

IR (film): ν = 2942, 2917 (CH), 1603, 1551 (P≡C), 1460, 851, 738 cm^{-1}.

^{31}P NMR (C_6D_6): δ = 2.5 (s).

^{1}H NMR (C_6D_6): δ = 1.98 (s, 3H, *p*-CH_3), 2.39 (s, 6H, *o*-CH_3), 6.56 (s, 2H, aryl-H).

^{13}C NMR (C_6D_6): δ = 21.6 (s, *o*-CH_3), 21.8 (s, *p*-CH_3), 128.3 (d, ^4J(C,P) = 2.1 Hz, *m*-C), 129.5 (s, *p*-C), 139.6 (d, ^3J(C,P) = 6.2 Hz, *o*-C), 142.7 (d, ^2J(C,P) = 6.9 Hz, *i*-C), 163.4 [d, ^1J(C,P) = 45.8 Hz, P≡C].

MS (EI, 70 eV): *m/z* (%) = 162 (100.0) [M^+], 147 (78.8) [$M^+ - CH_3$], 133 (10.9) [$MesCP^+ - CH_2 - CH_3$], 129 (21.4), 115 (14.0), 119 (12.2) [Mes^+], 91 (3.0) [$C_6H_4CH_3^+$], 77 (5.2) [$C_6H_5^+$].

$C_{10}H_{11}P$	calcd	C	74.06	H	6.84
(162.17)	found		73.80		6.88

5-Mesityl-1*H*-1,2,4-diazaphospholes 6a,b; General Procedure:

To a magnetically stirred solution of phosphaalkyne **1b** in Et_2O (3 mL) at –78 °C was added dropwise a solution of α-diazo ester **4** in Et_2O (2 mL). After the mixture had been allowed to warm up to r.t. over a period of 24 h, all volatile components were removed at 25 °C/10^{-3} mbar. The purification of the residue was achieved by column chromatography (silica gel, pentane/Et_2O 3:1) to give **6a,b**.

Methyl 5-Mesityl-1*H*-1,2,4-diazaphosphole-3-carboxylate (6a):

From methyl diazoacetate **(4a)** (62 mg, 0.62 mmol) and phosphaalkyne **1b** (100 mg, 0.62 mmol), **6a** was obtained as a yellow oil; yield: 108 mg (67%).

IR (Et_2O): ν = 3165 (NH), 2995–2800, 1723 (CO), 1440, 1350, 1324, 1152 cm^{-1}.

^{31}P NMR (C_6D_6): δ = 105.7 (s).

^{1}H NMR ($CDCl_3$): δ = 2.04 (s, 6H, *o*-CH_3), 2.21 (s, 3H, *p*-CH_3), 3.93 (s, 3H, OCH_3), 6.92 (s, 2H, aryl-H), 11.36 (s, 1H, NH).

^{13}C NMR ($CDCl_3$): δ = 20.5 [d, ^5J(C,P) = 1.6 Hz, *o*-CH_3], 20.8 (s, *p*-CH_3), 52.45 (s, OCH_3), 128.2 [d, ^2J(C,P) = 14.5 Hz, *i*-C, Mes], 128.4 (s, *m*-C, Mes), 137.2 [d, ^3J(C,P) = 3.2 Hz, *o*-C, Mes], 139.1 (s, *p*-C, Mes), 163.4 [d, ^2J(C,P) = 22.5 Hz, CO], 167.9 [d, ^1J(C,P) = 61.0 Hz, C3/5], 175.3 [d, ^1J(C,P) = 53.8 Hz, C3/5].

MS (EI, 70 eV): *m/z* (%) = 262 (100.0) [M^+], 219 (27.8) [$M^+ - N_2 - CH_3$], 175 (44.9) [$M^+ - N_2 - CO_2CH_3$], 144 (43.7) [$MesCCH^+$], 91 (28.0) [$C_6H_4CH_3^+$], 77 (11.6) [$C_6H_5^+$].

$C_{13}H_{15}N_2O_2P$	calcd	C	59.54	H	5.76	N	10.68
(262.25)	found		59.52		5.80		10.12

Ethyl 5-Mesityl-1*H*-1,2,4-diazaphosphole-3-carboxylate (6b):

From ethyl diazoacetate **(4b)** (70 mg, 0.62 mmol) and phosphaalkyne **1b** (100 mg, 0.62 mmol), **6b** was obtained as a yellow oil; yield: 124 mg (73%).

IR (CH_2Cl_2): ν = 3369 (NH), 3298, 3216, 2990–2800, 1748, 1723, 1467, 1446, 1383, 1199, 1165, 1110 cm^{-1}.

^{31}P NMR (C_6D_6): δ = 106.0 (s).

^{1}H NMR ($CDCl_3$): δ = 1.42 [t, 3H, ^3J(H,H) = 7.2 Hz, CH_2CH_3], 2.07 (s, 6H, *o*-CH_3), 2.27 (s, 3H, *p*-CH_3), 4.45 [q, 2H, ^3J(H,H) = 7.1 Hz, CH_2CH_3], 6.94 (s, 2H, aryl-H), 10.45 (s, 1H, NH).

^{13}C NMR ($CDCl_3$): δ = 14.3 (s, CH_2CH_3), 20.6 (s, *o*-CH_3), 21.0 (s, *p*-CH_3), 61.7 (s, CH_2CH_3), 128.9 [d, ^2J(C,P) = 14.5 Hz, *i*-C, Mes], 128.4 (s, *m*-C, Mes), 137.2 [d, ^3J(C,P) = 3.2 Hz, *o*-C, Mes], 139.1 (s, *p*-C, Mes), 163.3 [d, ^2J(C,P) = 22.5 Hz, CO], 167.9 [d, ^1J(C,P) = 57.0 Hz, C3], 175.3 [d, ^1J(C,P) = 55.4 Hz, C5].

MS (EI, 70 eV): *m/z* (%) = 276 (100.0) [M^+], 219 (46.5) [$M^+ - N_2 - CH_2CH_3$], 177 (60.0) [MesCPNH$^+$], 175 (63.8) [$M^+ - N_2 - CO_2CH_2CH_3$], 144 (56.3) [MesCCH$^+$], 91 (19.4) [$C_6H_4CH_3^+$], 77 (15.5) [$C_6H_5^+$], 57 (24.6) [$COCH_2CH_3^+$].

5-Mesityl-1,2,3,4-triazaphospholes 8a–c; General Procedure:
To a magnetically stirred solution of phosphaalkyne **1b** (0.62 mmol) in Et_2O (3 mL) at –78 °C was added dropwise the azide **7a** in pentane (3 mL) or **7b,c** (0.62 mmol) in Et_2O (2 mL). The solution was allowed to warm up to r.t. and stirred for 24 h. All volatile components were removed at 25 °C/10^{-3} mbar. Purification of the crude materials was as described below.

5-Mesityl-3-methyl-1,2,3,4-triazaphosphole (8a):
From methyl azide **(7a)** (140 mg, 2.5 mmol) and phosphaalkyne **1b** (324 mg, 2.0 mmol) **8a** was obtained after bulb-to-bulb distillation (160 °C/10^{-2} mbar) as a yellow oil; yield: 410 mg (93%).
IR (film): ν = 2943, 2915, 1610, 1440, 1375, 1235, 1188, 1008, 853, 813, 684 cm^{-1}.
^{31}P NMR ($CDCl_3$): δ = 182.5 (s).
^{1}H NMR ($CDCl_3$): δ = 2.08 (s, 6H, *o*-CH_3), 2.31 (s, 3H, *p*-CH_3), 4.28 [d, ^3J(H,P) = 6.6 Hz, 3H, NCH_3], 6.91 (s, 2H, aryl-H).
^{13}C NMR ($CDCl_3$): δ = 21.0 (s, *p*-CH_3), 21.1 (s, *o*-CH_3), 38.5 [d, ^2J(C,P) = 15.7 Hz, NCH_3], 128.3 (s, *m*-C), 128.9 [d, ^2J(C,P) = 18.0 Hz, *i*-C], 136.5 [d, ^3J(C,P) = 3.9 Hz, *o*-C], 137.8 (s, *p*-C), 181.0 [d, ^1J(C,P) = 49.0 Hz, C5].

$C_{11}H_{14}N_3P$	calcd	C	60.27	H	6.44	N	19.17
(219.23)	found		60.30		6.39		19.20

3-Butyl-5-mesityl-1,2,3,4-triazaphosphole (8b):
From butyl azide **(7b)** (62 mg, 0.62 mmol) and phosphaalkyne **1b** (100 mg, 0.62 mmol), **8b** was obtained after chromatography (silica gel, pentane/Et_2O 3:1) after evaporation at 25 °C/10^{-3} mbar as a yellow oil; yield: 121 mg (75%).
IR (film): ν = 2958, 2872, 2854, 1612, 1457, 1376, 1208, 1033, 1002, 851, 735 cm^{-1}.
^{31}P NMR (C_6D_6): δ = 178.4 (s).
^{1}H NMR (C_6D_6): δ = 1.00 [t, 3H, ^3J(H,H) = 6.5 Hz, $CH_2CH_2CH_2CH_3$], 1.39–1.49 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.00–2.08 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.11 (s, 6H, *o*-CH_3), 2.33 (s, 3H, *p*-CH_3), 4.67 (pseudo-q, 2H, $CH_2CH_2CH_2CH_3$), 6.97 (s, 2H, aryl-H).
^{13}C NMR ($CDCl_3$): δ = 13.4 (s, $CH_2CH_2CH_2CH_3$), 19.7 (s, $CH_2CH_2CH_2CH_3$), 20.9 (s, *p*-CH_3), 21.0 [d, ^4J(C,P) = 2.4 Hz, *o*-CH_3], 34.3 [d, ^3J(C,P) = 3.2 Hz, $CH_2CH_2CH_2CH_3$], 52.2 [d, ^2J(C,P) = 11.3 Hz, $CH_2CH_2CH_2CH_3$], 128.4 (s, *m*-C, Mes), 129.2 [d, ^2J(C,P) = 18.5 Hz, *i*-C, Mes], 136.8 [d, ^3J(C,P) = 4.0 Hz, *o*-C, Mes], 138.0 (s, *p*-C, Mes), 180.7 [d, ^1J(C,P) = 49.8 Hz, C_5].
MS (EI, 70 eV): *m/z* (%) = 261 (22.3) [M^+], 219 (29.4) [$M^+ - N_3$], 177 (93.7), 162 (22.1) [MesCP$^+$], 144 (63.2) [MesCCH$^+$], 119 (32.6) [Mes$^+$], 91 (28.4) [$C_6H_4CH_3^+$], 77 (20.3) [$C_6H_5^+$], 57 (44.9) [*n*-Bu$^+$].

$C_{14}H_{20}N_3P$	calcd	C	64.35	H	7.71	N	16.08
(261.31)	found		64.19		7.82		15.97

5-Mesityl-3-(4-nitrophenyl)-1,2,3,4-triazaphosphole (8c):
From 4-nitrophenyl azide (**7c**; 101 mg, 0.62 mmol) and phosphaalkyne **1b** (100 mg, 0.62 mmol), **8c** was obtained after chromatography (silica gel, pentane/Et_2O 3:1) and evaporation of the eluent at 25 °C/10^{-3} mbar as a yellow oil; yield: 139 mg (69%).
IR (CH_2Cl_2): ν = 3776, 3076, 2999, 2963, 1596 (NO_2), 1529 (NO_2), 1495, 1351, 1255, 1035, 854, 805 cm^{-1}.
^{31}P NMR (C_6D_6): δ = 177.7 (s).
^{1}H NMR (C_6D_6): δ = 2.17 (s, 6H, *o*-CH_3), 2.35 (s, 3H, *p*-CH_3), 7.02 (s, 2H, aryl-H, Mes), 8.14–8.17 (m, 2H, *o*-H, Ph), 8.40–8.42 (m, 2H, *m*-H, Ph).
^{13}C NMR ($CDCl_3$): δ = 21.1 (s, *p*-CH_3), 21.2 [d, ^4J(C,P) = 2.4 Hz, *o*-CH_3], 122.0 [d, ^2J(C,P) = 8.0 Hz, *o*-C, Ph], 125.4 (s, *m*-C, Ph), 128.0 [d, ^2J(C,P) = 17.7 Hz, *i*-C, Mes], 128.8 (s, *m*-C, Mes), 136.9 [d, ^3J(C,P) = 4.0 Hz, *o*-C, Mes], 138.9 (s, *p*-C, Mes), 145.2 [d, ^2J(C,P) = 9.4 Hz, *i*-C, Ph], 147.1 (s, *p*-C, Ph), 182.2 [d, ^1J(C,P) = 49.8 Hz, P=C].
MS (EI, 70 eV): *m/z* (%) = 326 (1.8) [M^+], 298 (100.0) [$M^+ - N_2$], 297 (42.2) [$M^+ - N_2 - H$], 251 (52.1) [$M^+ - N_2 - H - NO_2$], 236 (20.6) [$M^+ - N_2 - H - NO_2 - CH_3$], 147 (12.9) [MesCP$^+ - CH_3$].

$C_{16}H_{15}N_4O_2P$	calcd	C	58.89	H	4.63	N	17.17
(326.30)	found		58.87		4.61		17.06

5-Mesityl-3-phenyl-1,2,4-oxazaphosphole (10a):
To a solution of phosphaalkyne **1b** (324 mg, 2.00 mmol) and triethylamine (250 mg, 2.50 mmol) in Et_2O (10 mL) a solution of benzohydroxamic acid chloride (310 mg, 2.00 mmol) in Et_2O (5 mL) was added dropwise at 0 °C. Stirring was continued for 1 h at the same temperature. After separation of the precipitate by filtration the solvent was removed at 25 °C/10^{-3} mbar. Bulb-to-bulb distillation (200 °C/10^{-2} mbar) furnished **10a** as a colorless oil; yield: 510 mg (90%).
IR (film): ν = 2960, 2930, 1615, 1465, 1317, 1270, 1145, 1005, 855, 765, 695, 680 cm^{-1}.
^{31}P NMR ($CDCl_3$): δ = 82.9 (s).
^{1}H NMR (C_6D_6): δ = 2.23 (s, 3H, *o*-CH_3), 2.30 (s, 6H, *p*-CH_3), 6.94 (s, 2H, aryl-H, Mes), 7.30–8.10 (m, 5H, aryl-H, Ph).

$C_{17}H_{16}NOP$	calcd	C	72.59	H	5.73	N	4.98
(281.29)	found		72.30		5.75		4.50

3,5-Dimesityl-1,2,4-oxazaphosphole (10b):
At –78 °C a solution of mesitylcarbonitrile oxide **(9b)** (69 mg, 0.43 mmol) in toluene (3 mL) was added dropwise to a stirred solution of **1b** (70 mg, 0.43 mmol) in toluene (2 mL). The mixture was allowed to warm up to 25 °C overnight and the solvent was then removed at 25 °C/10^{-3} mbar. The colorless residue was washed with cold pentane affording the 1,2,4-oxazaphosphole **10b** as a colorless powder which was crystallized from Et_2O at –30 °C; yield: 124 mg (89%), mp 155 °C (dec.).
IR (pentane): ν = 1413, 1380, 1099, 1019, 866, 850, 807, 730, 703, 668 cm^{-1}.
^{31}P NMR (C_6D_6): δ = 92.2 (s).
^{1}H NMR (C_6D_6): δ = 2.07, 2.13 (each s, 3H, *p*-CH_3), 2.19, 2.23 (each s, 6H, *o*-CH_3), 6.70, 6.77 (each s, 2H, aryl-H).
^{13}C NMR ($CDCl_3$): δ = 20.4, 20.5 (each s, *o*-CH_3), 21.1, 21.1 (each s, *p*-CH_3), 127.4 [d, ^2J(C,P) = 5.1 Hz, *i*-C], 127.7 (s, *i*-C), 128.5, 128.7 (each s, *m*-C), 136.4 [d, ^3J(C,P) = 2.6 Hz, *o*-C], 137.0 [d, ^3J(C,P) = 4.2 Hz, *o*-C], 138.6, 139.8 (each s, *p*-C), 180.0 [d, ^1J(C,P) = 62.7 Hz, C3], 210.2 [d, ^1J(C,P) = 58.5 Hz, C5].
MS (EI, 70 eV): *m/z* (%) = 323 (6.7) [M^+], 178 (10.9) [M^+ – MesCN], 147 (100.0) [MesCO$^+$], 145 (5.0) [MesCN$^+$], 119 (12.2) [Mes$^+$].

$C_{20}H_{22}NOP$	calcd	C	74.29	H	6.86	N	4.33
(323.37)	found		74.46		6.66		4.37

4-Mesityl-1-methyl-2,5-diphenyl-1,3-azaphosphole (12); Typical Procedure:
To a magnetically stirred solution of phosphaalkyne **1b** (100 mg, 0.62 mmol) in toluene (2 mL) at r.t. was added dropwise a solution of the münchnone **11** (155 mg, 0.62 mmol) in toluene (1 mL). After the mixture had been heated at 55 °C for 6 d, the volatile components were removed at 25 °C/10^{-3} mbar and the remaining oil was purified by column chromatography (silica gel, pentane/Et_2O 20:1) to give **12** as a yellow oil; yield: 105 mg (46%).
IR (CH_2Cl_2): ν = 3081, 2960, 2922, 1474, 1446, 1353, 1257, 1074, 1020, 856, 808 cm^{-1}.
^{31}P NMR (C_6D_6): δ = 106.0 (s).
^{1}H NMR ($CDCl_3$): δ = 2.19 (s, 6H, *o*-CH_3), 2.30 (s, 3H, *p*-CH_3), 3.64 (s, 3H, NCH_3), 6.86 (s, 2H, aryl-H, Mes), 7.21–7.56 (m, 10H, aryl-H, Ph).
^{13}C NMR ($CDCl_3$): δ = 21.0 (s, *p*-CH_3), 21.5 (s, *o*-CH_3), 37.9 (s, NCH_3), 127.6 (s, aryl-C), 127.7 (s, aryl-C), 127.8 (s, aryl-C), 128.1 (s, aryl-C), 128.3 (s, aryl-C), 129.5 [d, ^2J(C,P) = 8.0 Hz, aryl-C], 129.7 (s, aryl-C), 133.8 [d, ^2J(C,P) = 15.3 Hz, aryl-C], 134.0 (s, aryl-C),

135.6 (s, aryl-C), 135.7 (s, aryl-C), 136.9 [d, ^2J(C,P) = 3.3 Hz, aryl-C], 141.3 [d, ^1J(C,P) = 43.8 Hz, C4], 142.1 [d, ^2J(C,P) = 4.6 Hz, C5], 170.8 [d, ^1J(C,P) = 47.1 Hz, C2].
MS (EI, 70 eV): *m/z* (%) = 369 (40.3) [M^+], 251 (43.0) [M^+ – Mes + H], 118 (100.0) [Mes^+ – H], 91 (7.4) [$C_6H_4CH_3^+$], 77 (29.4) [$C_6H_5^+$].

4-Mesityl-2,5-diphenyl-1,3-thiaphosphole (14):
The reaction and workup of phosphaalkyne **1b** (100 mg, 0.62 mmol) in toluene (2 mL) and the mesoionic compound **13** (157 mg, 0.62 mmol) in toluene (1 mL) were analogous to the preceding procedure and furnished **14** as a yellow oil; yield: 135 mg (59%).
IR (Et_2O): ν = 2976, 2944, 2923, 2840, 1474, 1449, 1378, 850, 756, 691 cm^{-1}.
^{31}P NMR (C_6D_6): δ = 217.5 (s).
^{1}H NMR (C_6D_6): δ = 2.11 (s, 6H, *o*-CH_3), 2.33 (s, 3H, *p*-CH_3), 6.91 (s, 2H, aryl-H, Mes), 7.24–7.40 (m, 10H, aryl-H, Ph).
^{13}C NMR ($CDCl_3$): δ = 21.1 (s, *p*-CH_3), 21.2 (s, *o*-CH_3), 125.9 [d, ^2J(C,P) = 13.3 Hz, aryl-C], 128.0 (s, aryl-C), 128.2 (s, aryl-C), 128.4 [d, ^2J(C,P) = 2.0 Hz, aryl-C], 128.5 (s, aryl-C), 129.0 (s, aryl-C), 133.2 [d, ^2J(C,P) = 19.2 Hz, aryl-C], 134.1 (s, aryl-C), 136.3 (s, aryl-C), 136.4 [d, ^2J(C,P) = 4.0 Hz, aryl-C], 136.5 (s, aryl-C), 136.9 (s, aryl-C), 150.3 [d, ^2J(C,P) = 10.0 Hz, C5], 157.5 [d, ^1J(C,P) = 46.4 Hz, C4], 177.4 [d, ^1J(C,P) = 58.4 Hz, C2].
MS (EI, 70 eV): *m/z* (%) = 372 (33.3) [M^+], 340 (6.9) [M^+ – S], 147 (31.0) [$MesCP^+$ – CH_3], 119 (23.5) [Mes^+], 91 (30.7) [$C_6H_4CH_3^+$], 77 (39.9) [$C_6H_5^+$], 73 (100.0), 57 (69.7).

2-Mesityl-1-phosphacyclohexa-1,4-diene (15):
At –78 °C buta-1,3-diene (700 mg, 12.9 mmol) was condensed into a pressure tube and a solution of phosphaalkyne **1b** (100 mg, 0.62 mmol) in toluene (3 mL) added. The mixture was allowed to warm to r.t. and then heated for 2 d at 55 °C. After evaporation of the solvent and excess buta-1,3-diene at 25 °C/10^{-3} mbar a yellow/orange oily residue was obtained which could not be purified by bulb-to-bulb distillation (200 °C/10^{-3} mbar), by column chromatography (silica gel, pentane/Et_2O), or by crystallization (toluene).
^{31}P NMR (C_6D_6): δ = 215.7 (s).
MS (EI, 70 eV): *m/z* (%) = 216 (100.0) [M^+], 201 (17.0) [M^+ – CH_3], 162 (61.1) [$MesCP^+$], 147 (34.0) [$MesCP^+$ – Me], 119 (56.3) [Mes^+], 91 (27.2) [$C_6H_4CH_3^+$], 77 (5.7) [$C_6H_5^+$].

1-η^1-[2-Mesityl-1-phosphacyclohexa-1,4-diene]pentacarbonyltungsten (17):
Compound **15** (216 mg, 1.0 mmol) in THF (5 mL) was added to a solution of $W(CO)_5$•THF, prepared by irradiation of $W(CO)_6$ (387 mg, 1.1 mmol) in THF (60 mL). After 5 h at r.t. the solvent was removed at 25 °C/10^{-3} mbar, the oily residue was eluted with pentane (20 mL) and subjected to chromatography (silica gel, column: 1.8 × 30 cm, pentane 200 mL) to furnish a pale yellow oil, which crystallized from pentane at 2 °C; yield: 340 mg (63%); mp 97 °C.
IR (Et_2O): ν = 3030–2860, 2076(CO), 1992 (CO), 1668, 1611, 1567, 1467, 1463, 1459, 1263, 1164, 1005, 849, 746, 667, 621 cm^{-1}.
^{31}P NMR (C_6D_6): δ = 170.0 [s, ^1J(P,W) = 259.6 Hz].
^{1}H NMR (C_6D_6): δ = 2.10 (s, 6H, *o*-CH_3), 2.11 (s, 3H, *p*-CH_3), 2.40–2.48, 2.63–2.75 (each m, 4H, 3,6-CH_2), 5.17–5.26, 5.40–5.46 (each m, 2H, H4,5), 6.77 (s, 2H, aryl-H).
^{13}C NMR ($CDCl_3$): δ = 19.6 (s, *o*-CH_3), 21.0 (s, *p*-CH_3), 31.4 [d, ^2J(C,P) = 2.6 Hz, C3], 37.5 [d, ^1J(C,P) = 9.3 Hz, C6], 120.3 [d, ^3J(C,P) = 8.5 Hz, C4], 125.4 [d, ^2J(C,P) = 11.9 Hz, C5], 129.2 (s, *m*-C, Mes), 134.9 [d, ^2J(C,P) = 12.7 Hz, *i*-C, Mes], 137.7 (s, *p*-C, Mes), 137.9 [d, ^4J(C,P) = 3.4 Hz, *o*-C, Mes], 181.4 [d, ^1J(C,P) = 47.5 Hz, C2], 194.5 [d, ^2J(C,P) = 9.8 Hz, ^1J(C,W) = 124.2 Hz, COeq], 198.8 [d, ^2J(C,P) = 28.8 Hz, ^1J(C,W) = 45.8 Hz, COax].
MS (EI, 57 eV): *m/z* (%) = 540 (53.0) [M^+], 484 (30.4) [M^+ – 2 CO], 456 (35.2) [M^+ – 3 CO], 428 (75.9) [M^+ – 4 CO], 426 (85.6) [M^+ – 3 CO – 2 CH_3], 400 (49.1) [M^+ – 5 CO], 398 (96.2) [M^+ – 4 CO – 2 CH_3], 396 (100), 393 (27.1) [M^+ – CO – Mes], 199 (15.4) [$MesCPC_4H_4^+$ – CH_3], 91 (16.7) [$C_6H_4CH_3^+$], 77 (11.7) [$C_6H_5^+$], 56 (23.2) [$C_4H_6^+$], 55 (63.6) [$C_4H_5^+$].

$C_{19}H_{17}O_5PW$	calcd	C	42.25	H	3.17
(326.30)	found		41.79		3.15

2,8-Dimesityl-1,7-diphosphatricyclo[3.2.1.0^{2,7}]oct-3-ene (18):
A solution of phosphaalkyne **1b** (134 mg, 0.62 mmol) in toluene (2 mL) was stirred at 55 °C for 1 week. The solvent was then removed at 25 °C/10^{-3} mbar. Further purification of the orange, oily residue by bulb-to-bulb distillation (50 – 250 °C/10^{-3} mbar) or by column chromatography (silica gel, pentane/Et_2O) was not possible due to unselective decomposition.
^{31}P NMR (C_6D_6): δ = –168.0 [d, ^1J(P,P) = 158.3 Hz], –163.1 [d, ^1J(P,P) = 158.3 Hz].
MS (EI, 70 eV): *m/z* (%) = 378 (42.9) [M^+], 363 (13.0) [M^+ – CH_3], 216 (100.0) [M^+ – MesCP], 162 (44.5) [$MesCP^+$], 119 (13.8) [Mes^+], 91 (16.7) [$C_6H_4CH_3^+$], 77 (11.2) [$C_6H_5^+$].

Methyl 1,5,6-Tri-*tert*-butyl-3-mesityl-2-phosphabicyclo[2.2.0]hexa-2,5-diene-4-carboxylate (20):
To a magnetically stirred solution of cyclobutadiene **19** (172 mg, 0.62 mmol) in pentane (3 mL) at –78 °C was added dropwise a solution of phosphaalkyne **1b** (100 mg, 0.62 mmol) in pentane (3 mL). The mixture was then allowed to warm to 25 °C over 4 h and stirred for 2 h at r.t. The volatile components were removed at 25 °C/10^{-3} mbar. Purification of the remaining oil **20** was not possible by bulb-to-bulb distillation (50–250 °C/10^{-3} mbar) due to thermal decomposition.
^{31}P NMR (C_6D_6): δ = 335.9 (s).
^{1}H NMR (C_6D_6): δ = 1.23, 1.26, 1.41 (each s, each 9H, *t*-Bu), 2.15 (s, 3H, *p*-CH_3), 2.42 (s, 6H, *o*-CH_3), 3.20 (s, 3H, OCH_3), 6.85 (s, 2H, aryl-H).
^{13}C NMR ($CDCl_3$): δ = 21.1 (s, *p*-CH_3), 22.8 (s, *o*-CH_3), 50.8 (s, OCH_3), 72.8 [d, ^1J(C,P) = 19.3 Hz, C1], 78.5 [d, ^2J(C,P) = 5.6 Hz, C4], 136.3(s, *m*-C, Mes), 138.4 [d, ^4J(C,P) = 5.6 Hz, *o*-C, Mes], 147.5 (s, *p*-C, Mes), 152.7 [d, ^2J(C,P) = 20.1 Hz, C6], 158.8 [d, ^3J(C,P) = 5.6 Hz, C5], 172.0 [d, ^3J(C,P) = 4.8 Hz, CO], 224.0 [d, ^1J(C,P) = 29.7 Hz, C3].
Due to impurities the remaining data could not be assigned.
MS (EI, 70 eV): *m/z* (%) = 440 (48.6) [M^+], 425 (8.3) [M^+ – CH_3], 243 (78.7) [M^+ – *t*-BuCC*t*-Bu, – CO_2CH_3], 207 (64.6) [M^+ – MesCP – CCO_2CH_3], 147 (19.3) [$MesCP^+$ – CH_3], 119 (8.1) [Mes^+], 84 (100.0) [*t*-$BuCHCH_2^+$], 57 (89.6) [*t*-Bu^+].

4,5,6-Tri-*tert*-butyl-2-mesityl-1-aza-3-phosphabicyclo[2.2.0]-hexadiene (22):
A solution of tri-*tert*-butylazete **(21)** (80 mg, 0.36 mmol) in pentane (2 mL) was added dropwise to a solution of phosphaalkyne **1b** (59 mg, 0.36 mmol) at –78 °C in pentane (4 mL). Warming to r.t. overnight was followed by removal of the solvent at 25 °C/10^{-3} mbar. The residue was extracted with pentane (5 mL) and then separated from insoluble material by filtration through a D3 sinter filled with Celite. Removal of the solvent at 25 °C/10^{-3} mbar furnished **21** as a colorless powder; yield: 127 mg (91%).
^{31}P NMR (C_6D_6): δ = 230.4 (s).
^{1}H NMR (C_6D_6): δ = 0.98, 1.25, 1.28 (each s, each 9H, *t*-Bu), 2.06 (s, 3H, CH_3), 2.42 [d, ^5J(C,P) = 2.0 Hz, 3H, *o*-CH_3], 2.70 (s, 3H, CH_3), 6.74, 6.77 (each s, 2H, aryl-H).
^{13}C NMR ($CDCl_3$): δ = 21.5 (s, *p*-CH_3), 22.7 (s, *o*-CH_3), 27.9 [d, J(C,P) = 3.4 Hz, C(CH_3)$_3$], 30.0, 30.7 [each s, C(CH_3)$_3$], 31.3, 34.0 [each s, *C*(CH_3)$_3$], 36.7 [d, J(C,P) = 5.1 Hz, *C*(CH_3)$_3$], 89.7 [d, ^1J(C,P) = 23.7 Hz, C4], 127.6 (s, *m*-C), 128.8 [d, ^2J(C,P) = 12.7 Hz, *i*-C], 137.4 [d, ^3J(C,P) = 5.1 Hz, *o*-C], 137.8 (s, *p*-C), 139.5 [d, ^2J(C,P) = 3.4 Hz, C5], 162.1 [d, ^3J(C,P) = 19.5 Hz, C6], 225.9 [d, ^1J(C,P) = 37.3 Hz, C2].
MS (EI, 70 eV): *m/z* (%) = 383 (6.7) [M^+], 178 (10.9) [M^+ – MesCN], 147 (100.0) [$MesCO^+$], 145 (5.0) [$MesCN^+$], 119 (12.2) [Mes^+].

X-ray Crystal Structure Analysis of 17:

Crystal data: $C_{19}H_{17}OPW$, M_r = 540.15; triclinic; space group P; a = 757.34(10), b = 1063.93(7), c = 1366.9(2) pm, α = 71.080(10)°, β = 84.993(9)°, χ = 75.304(10)°, V = 1.0078 (2) nm^3; Z = 2, d_c = 1.780 Mg/m^3.

Data collection: The data collection was performed using an automatic four circle diffractrometer (Siemens P 4) at r.t.. Crystal dimensions: 0.45 × 0.30 × 0.15 mm. The measurements were made in the range1.57<Θ <25.00°, λ = 0.71073 MoKα (graphite monochromator), $-1 \le h \le 8$, $-11 \le k \le 11$, $-16 \le l \le 16$, a total of 4457 reflections, of which 3458 were independent reflections.

Structure solution and refinement: The structure was solved using direct methods (SHELXS-86)[40] and refined with the full matrix least squares procedure against F^2 (SHELXL-93)[41]. The anisotropic refinement converged at R1 = 0.0280 and wR2 = 0.0742 [I>2σ(I)] and R1 = 0.0327, wR2 = 0.0907 [all data]. The difference Fourier synthesis on the basis of the final structural model showed a maximum of 729 e/nm^3 and a minimum of –695 e/nm^3.[42]

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(1) Part 128, see: Simon, J.; Bergsträßer, U.; Regitz, M. *J. Chem. Soc., Chem. Commun.* **1998**, 867.
(2) Regitz, M. *Angew. Chem.* **1988**, *100*, 1541; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1484.
(3) Regitz, M. *Chem. Rev.* **1990**, *90*, 191.
(4) Regitz, M. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; p 77.
(5) Regitz, M.; Hoffmann, A.; Bergsträßer, U. In *Modern Acetylene Chemistry*: Stang, P. J.; Diederich, F., Eds.; VCH: Weinheim, 1995; p 173.
(6) Appel, R.; Maier, G.; Reisenauer, H.-P.; Westerhaus, A. *Angew. Chem.* **1981**, *93*, 215; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 197.
(7) Märkl, G.; Sejpka, H. *Tetrahedron Lett.* **1986**, *27*, 171.
(8) Veeck, W. G.; Regitz, M. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 5; p 1151.
(9) Breit, B.; Regitz, M. *Chem. Ber.* **1996**, *129*, 489.
(10) Fritz, G.; Hölderich, W. *Z. Anorg. Allg. Chem.* **1976**, *422*, 104.
(11) Barnes, R. P. *Org. Synth.* **1941**, *21*, 77.
(12) Becker, G. *Z. Anorg. Allg. Chem.* **1977**, *430*, 66.
(13) Mackewitz, T. W.; Regitz, M. *Synthesis* **1998**, 125.
(14) Mack, A.; Regitz, M. *Chem. Ber.* **1997**, *130*, 823.
(15) Rösch, W.; Regitz, M. *Angew. Chem.* **1984**, *96*, 898; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 903.
Rösch, W.; Facklam, T.; Regitz, M. *Tetrahedron* **1987**, *43*, 3247.
(16) Rösch, W.; Hees, U.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1645.
(17) Nyulászi, L.; Várnai, P.; Eisfeld, W.; Regitz, M. *J. Comput. Chem.* **1997**, *18*, 609.
(18) Rösch, W.; Regitz, M. *Synthesis* **1987**, 689.
(19) Rösch, W.; Richter, H.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1809.
(20) An exact assigment to C2 or C4 is not possible.
(21) Fuchs, E. P. O.; Rösch, W.; Regitz, M. *Angew. Chem.* **1987**, *99*, 1058; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1011.
Heydt, H.; Bergsträßer, U.; Fäßler, R.; Fuchs, E. P. O.; Kamel, N.; Mackewitz, T. W.; Michels, G.; Rösch, W.; Regitz, M.; Mazerolles, P.; Laurent, C.; Faucher, A. *Bull. Soc. Chim. Fr.* **1995**, *132*, 652.
(22) When the reaction of **1a** with buta-1,3-diene is carried out at 55 °C, 2-*tert*-butyl-1-phosphacyclohexa-1,4-diene (**15**, *t*-Bu instead of Mes) can be detected spectroscopically (^{31}P δ = 204.1). However, no isolation is possible as the subsequent ene reaction/[4+2] cycloaddition process is much faster for the *tert*-butyl derivative **1a** than for the mesitylphosphaacetylene **(1b)**.
(23) Marinetti, A.; Le Floch, P.; Mathey, F. *Organometallics* **1991**, *10*, 1190.
(24) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.
(25) Appel R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; p 157.
(26) Wingert, H.; Regitz, M. *Chem. Ber.* **1986**, *119*, 244.
Maier, G.; Bauer, J.; Huber-Patz, U.; Jahn, R.; Kallfaß, D.; Rodewald, H.; Irngartinger, H. *Chem. Ber.* **1986**, *119*, 1111.
Wingert, H.; Regitz, M.; *Z. Naturforsch. B* **1986**, *41*, 1306.
Wingert, H.; Maas, G.; Regitz, M. *Tetrahedron* **1986**, *42*, 5341.
(27) Fink, J.; Rösch, W.; Vogelbacher, U.-J.; Regitz, M. *Angew. Chem.* **1986**, *98*, 265; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 280.
(28) Vogelbacher, U.-J.; Ledermann, M.; Schach, T.; Michels, G.; Hees, U.; Regitz, M. *Angew. Chem.* **1988**, *100*, 304; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 272.
(29) Regitz, M.; Hocker, J.; Liedhegener, A. *Org. Synth. Coll. Vol. V* **1968**, *48*, 36.
(30) Searle, N. E. *Org. Synth.* **1953**, *36*, 25.
(31) Dimroth, O.; Wislicensius, W. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1573.
(32) Boyer, J. H.; Hamer, H. *J. Am. Chem. Soc.* **1955**, *77*, 951.
(33) Smith, P. A. S.; Bayer, J. H. *Org. Synth. Coll. Vol. IV* **1963**, 75.
(34) Grundmann, C.; Dean, J. M. *J. Org. Chem.* **1965**, *30*, 2809.
(35) Huisgen, R.; Gotthardt, H.; Bayer; H. O.; Schäfer, F. C. *Chem. Ber.* **1970**, *103*, 2611.
(36) Gotthardt, H.; Weishuhn, M. C.; Christl, B. *Chem. Ber.* **1976**, *109*, 740.
(37) Vogelbacher, U.-J.; Regitz, M.; Mynott, R. *Angew. Chem.* **1986**, *98*, 835; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 842.
(38) Weiland, H. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 1667.
(39) Strohmeier, W.; Müller, F.-J. *Chem. Ber.* **1969**, *102*, 3608.
(40) Sheldrick, G. M. *Fortran Program for the solution of Crystal Structures from Diffraction Data*; Institute for Organic Chemistry, University of Göttingen, 1986.
(41) Sheldrick, G. M. *Fortran Program for Crystal Structure Refinement*; Institute for Organic Chemistry, University of Göttingen, 1993.
(42) Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaflich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-408229, the authors, and the journal citation.