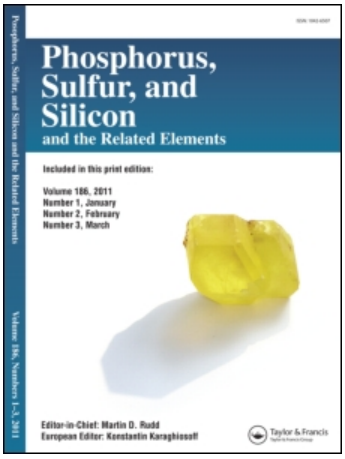

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OLIGOCYCLIC DERIVATIVES FROM THE PARTIAL BROMINATION OF 2-METHYL-5-PHENYL-1,2,4,3-TRIAZAPHOSPHOLE

Alfred Schmidpeter[a]; Helmut Tautz[a]; Franz Steinmüller[a]
[a] Institut für Anorganische Chemie der Universität München, München, Germany

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OLIGOCYCLIC DERIVATIVES FROM THE PARTIAL BROMINATION OF 2-METHYL-5-PHENYL-1,2,4,3-TRIAZAPHOSPHOLE

ALFRED SCHMIDPETER*, HELMUT TAUTZ and FRANZ STEINMÜLLER

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-80333 München, Germany

Dedicated in friendship to Professor Robert Wolf.

(Received 5 August 1996)

With less than one mol Br_2 per mol of the 2-methyl-5-phenyl-1,2,4,3-triazaphosphole (**1**) an equilibrium mixture forms, which contains besides **1** and its dimeric dibromide **3** at least three more components (**4**, **5**, **6**), which are intermediate between **1** and **3**. In **4**, **5** and **6** two, three and four triazaphosphole rings are connected to each other by PN bonds with the phosphorus atoms being in part tervalent, in part pentavalent.

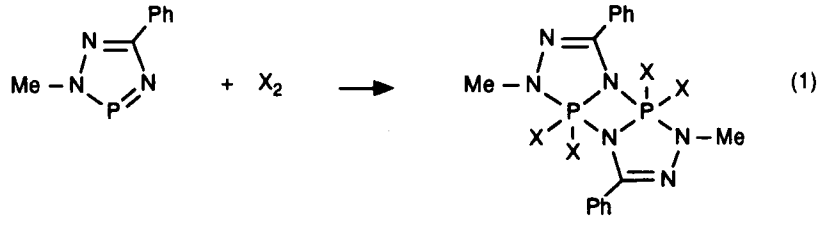
Secondary amines convert compounds **4** and **5** to the amino derivatives **11** and **12** of the same bi- and tricyclic structure. Of the bicyclic dimethylamino derivative **11b** a number of reactions are reported which all selectively involve the tervalent phosphorus only: Oxidation by bromine, elemental sulfur, phenyl azide and ethyl diazoacetate, insertion of CS_2, RNCS and RNCO into the exocyclic PN bond and formation of chelate complexes with $PdCl_2$ and $PtCl_2$. The same is shown by the reaction of the tricyclic piperidyl derivative **12c** with elemental sulfur.

Keywords: Triazaphospholes; oligocyclic structures; Staudinger reaction; heterocumulene insertion; chelating P/N-ligand; restricted PN rotation

BROMOSUBSTITUTED OLIGOCYCLIC TRIAZAPHOSPHOLES

Among the 1,2,4,3-triazaphospholes,[1–3] the 2-methyl-5-phenyl derivative **1** is the most investigated one. It adds one mole of chlorine or bromine to yield the dimers **2** and **3** of the respective 3,3-dihalo-triazaphospholes (equation 1).[4,5] The halogenation can be reverted *e.g.* by reaction with a dithiol.[4]

*Corresponding author.

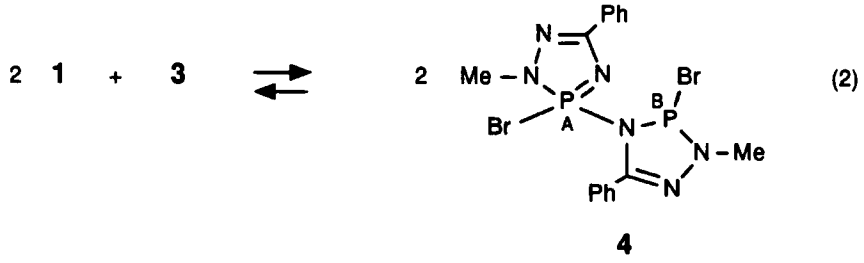


(1)

1 **2**, X = Cl
3, X = Br

With less than one mole bromine **1** reacts to give a number of products of the general formula $\mathbf{1}_n Br_2$, $n > 1$, intermediate between **1** and **3**. They form mixtures which reach equilibrium within a few minutes. The same mixtures of intermediates are obtained from the reaction of **1** and its dibromide **3**. In both cases the composition of the mixtures is determined by the molar ratio of the reactants. None of the intermediates can be isolated from the mixtures; in all attempts to do so, merely one of the terminal members is separated out and the equilibrium restores. Vacuum destillation removes the 1,2,4,3-triazaphosphole **1** as the most volatile component and leaves **3** as the residue, crystallization (from tetrachloromethane/pentane) removes **3** as the least soluble component and leaves **1** in solution.

The composition of the equilibrium mixtures can be monitored by their ^{31}P NMR spectra (Fig. 1). Two of the intermediates, $\mathbf{1}_2Br_2$ = **4** and $\mathbf{1}_3Br_2$ = **5**, are clearly identified by their AB and AB_2 spin systems, respectively (Table I). Their formation can be represented by equations (2) and (3). A third intermediate, $\mathbf{1}_4Br_2$ = **6**, is connected to **1** and **4** by an exchange process (equation 4) which involves only tervalent phosphorus and which is therefore more rapid than those involving pentavalent phosphorus. As it is rapid on the NMR time scale, its signals (representing an ABCD spin system) are not observed as such but averaged with those of **1** and **4** (Fig. 1).



(2)

4

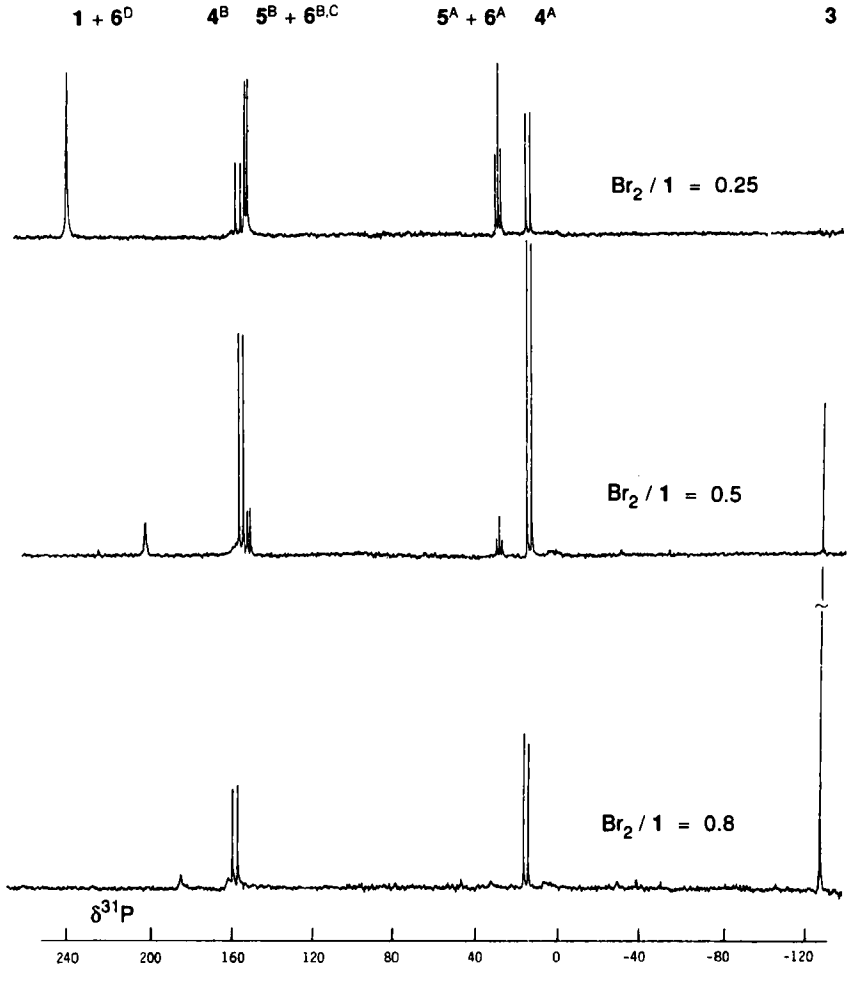
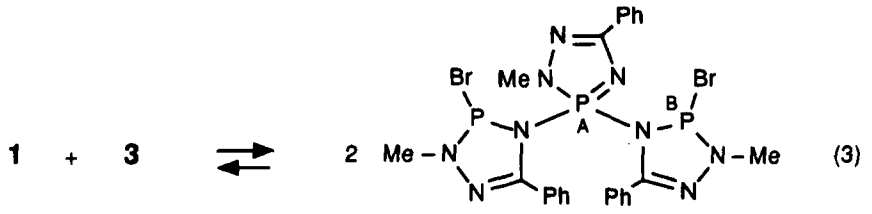


FIGURE 1 ^{31}P NMR Spectra of the equilibrium mixture

$$\mathbf{1} + Br_2 \rightleftarrows \mathbf{3}\ (= \mathbf{1}_2Br_4),\ \mathbf{4}\ (= \mathbf{1}_2Br_2),\ \mathbf{5}\ (= \mathbf{1}_3Br_2),\ \mathbf{6}\ (= \mathbf{1}_4Br_2)$$

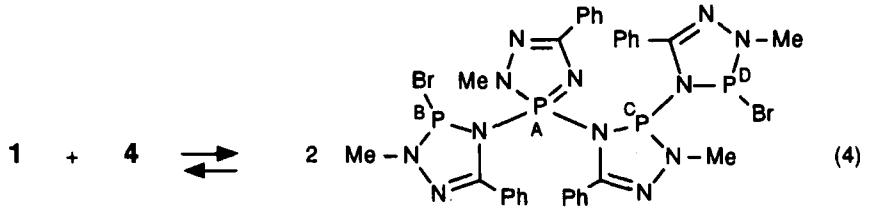
from a 1-molar chloroform solution of **1** and increasing amounts of bromine. Molar ratio Br_2/**1** = 0.25, 0.5 and 0.8. For the assignment of the different phosphorus atoms see equations (1) to (4).

The intermediates are built from two, three and four (and possibly more) triazaphosphole rings with the phosphorus ring members being partly still tervalent and three-coordinate ($\lambda^3\sigma^3P$), partly pentavalent and four-coordinate ($\lambda^5\sigma^4P$). As the ^{31}P chemical shifts in this series move decidedly to higher field with the phosphorus coordination number, the A and B signals of the interme-



(3)

5



(4)

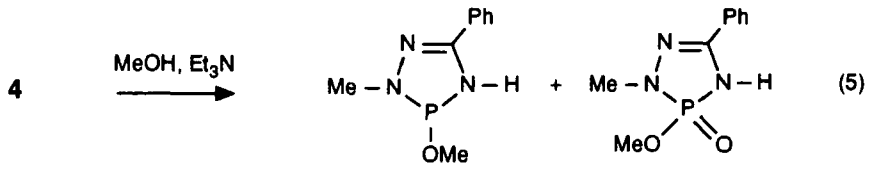
6

diates as well as the signals of the terminal members **1** with two-coordinate phosphorus ($\lambda^3\sigma^2$P) and **3** with five-coordinate phosphorus ($\lambda^5\sigma^5$P) appear well separated in the NMR spectra. The scale extends all the way from $\delta = 249$ to $\delta = -125$ (Fig. 1). The equilibrium mixtures are not stable but undergo a rearrangement reaction within a few days in which spirocyclic triazaphosphole derivatives are formed.[1,2,6]

AMINOSUBSTITUTED OLIGOCYCLIC TRIAZAPHOSPHOLES

In order to slow down the exchange processes (2)–(4) occurring in the equilibrium mixture and possibly to convert the generated oligocyclic systems of **4**, **5** and **6** into (meta)stable derivatives, we tried to replace the bromine for alkoxy and amino substituents. For this purpose mixtures with a Br_2/**1** ratio of 0.5 were used, made up according to equation (2) from **1** and **3** in a 2:1 molar ratio. In this mixture the share of **4** is at its maximum (characteristic composition in chloroform: **1** 3%, **6** 7%, **5** 9%, **4** 75%, **3** 7% of the triazaphosphole units and a still higher share of **4** in benzene).

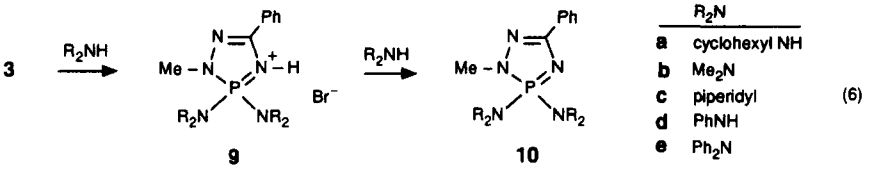
The reaction of this mixture with methanol in the presence of triethylamine yields, however, only the 3-methoxy-triazaphospholine **7** and its oxide **8** in equal amounts, obviously as the result of a complete dismutation of **4**. Compounds **7**

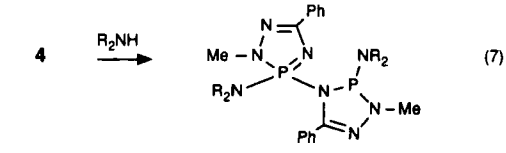


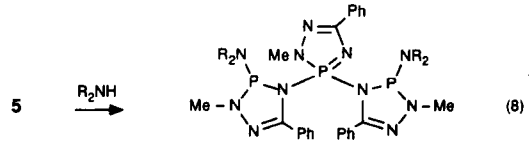
and **8** are known[5,7] from the addition of methanol to **1** and from the methanolysis of **2**, respectively.

Formation

In contrast, the reaction with primary or secondary amines generally yields amino derivatives of all the bromosubstituted species present in the equilibrium mixture except of the tetracyclic compound **6**. The equilibrium (4) obviously is too mobile for the substitution reaction to compete with.







The bicyclic and tricyclic structures, however, survive the substitution reactions (7) and (8) and gain stability as the amino derivatives **11** and **12**. Besides them the known monocyclic diamino-triazaphospholes **10**[5,8] are formed by equation (6) from **3** or by dismutation reactions from the other constituents. The

product distribution does not always correspond to the distribution of the bromo derivatives in the equilibrium mixture and similar conditions may give rather different preparative results. With cyclohexylamine **10a** and **11a** (Table II) were observed, but only **10a** was isolated. With dimethylamine **10b**, **11b** and **12b** were observed and the latter two were isolated. **11b** is used for further reactions (see below). It decomposes on heating according to equation (9).

$$\mathbf{11} \rightarrow \mathbf{1} + \mathbf{10} \tag{9}$$

With piperidine **10c**, **11c** and **12c** were observed and **12c** was isolated and is used for further reactions (see below). With aniline the hydrobromide **9d** was isolated and **12d** observed. Diphenylamine did react only with the help of the stronger base triethylamine to give **10e** and **11e**; **12e** was not observed.

^{31}P NMR Spectra

The ^{31}P chemical shift of the newly obtained 3,3-diamino-1,2,4,3λ^5-triazaphospholes **10a–e** is compared in Table I to the shift of known examples. It is clearly influenced by the nature of the amino substituents; for primary and phenylamino substituents δ^{31}P is found at significantly higher field (δ = 41–49) than for dialkylamino substituents (δ = 55–61).

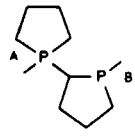
The bicyclic structure of compounds **4** and **11** becomes evident from their AB spin system (Table II). Although two diastereomers are possible for all of them, they are observed only for **11e**.

TABLE I ^{31}P chemical shift of 3-amino-2-methyl-5-phenyl-1,2,4,3λ^5-triazaphospholes

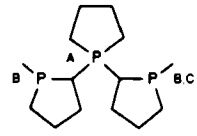
	R_2N	*Solvent*	*$\delta^{31}P$*	*Reference*
10	MeNH	$CDCl_3$	47.5	5
10a	cyclohexylNH	$CDCl_3$	45.0	
10b	Me_2N	$CDCl_3$	60.5	5
		CH_3CN	61.4	
10	$-CH_2NMe$	$CDCl_3$	55.4	5,8
10	Et_2N	C_6H_6	60.0	8,a
10c	piperidyl	C_6H_6	56.7	
10	morpholyl	C_6H_6	54.9	a
10d	PhNH	CH_3CN	48.9	
10e	Ph_2N	C_6H_6	41.2	
20	Me_2N/Br	$CDCl_3$	51.3	
21	Me_2N/O	$CDCl_3$	22.4	

[a]Prepared from equimolar amounts of **1** and I_2 and the double molar amount of the respective secondary amine in benzene solution.

TABLE II ^{31}P NMR chemical shifts δ_A, $\delta_{B,C}$ and coupling constants J_{AB}, J_{AC} = $^2J_{PP}$ [Hz] of bicyclic and tricyclic 1,2,4,3-triazaphosphole systems



4, 11, 13-17, 22-26



5, 12, 17, 18

	P-Substituents	*Solvent*		δ_A	$\delta_{B,C}$	$J_{AB,AC}$
4	Br	C_6H_6	AB	17.7	157.6	70.5
		$CHCl_3$	AB	11.6	151.6	71.9
5	Br	$CHCl_3$	AB_2	26.4	147.9	44.9
11a	cyclohexylNH	CH_3CN	AB	40.7	84.9	61.0
11b	Me_2N	$CDCl_3$	AB	47.8	100.9	50.4
11c	piperidyl	C_6H_6	AB	39.6	96.2	53.0
11e	Ph_2N	C_6H_6	AB	41.0	89.9	51.6[a]
			AB	42.0	89.4	65.7[a]
12b	Me_2N	$CDCl_3$	ABC	39.0	100.1	49.2
					102.4	49.2
12c	piperidyl	C_6H_6	ABC	39.8	93.1	51.9
					97.7	51.9
12d	PhNH	CH_3CN	ABC	36.6	76.3	56.3
					82.7	56.3
13	Me_2N, S	$CDCl_3$	AB	52.4	73.1	26.4
14	Me_2N, Se	$CDCl_3$	AB	52.6	68.2[b]	27.0
15	Me_2N, NPh	$CDCl_3$	AB	49.2	11.4	22.9
16	Me_2N, N_2CHCO_2Et	$CDCl_3$	AB	50.2	37.9	26.7
17	Me_2N, S	C_6H_6	ABC	42.5	95.9	60.6
					70.5	28.6
18	Me_2N, S	C_6H_6	ABC	37.4	66.1	26.7
					74.6	38.8
19	Me_2N, Br	$CDCl_3$	AB	33.3	22.3	22.1
22	Me_2N, Me_2NCS_2	C_6H_6	AB	46.6	101.1	43.3
23	Me_2N, $Me_2NCSNPh$	C_6H_6	AB	49.2	81.5	66.7
24	Me_2N, $Me_2NCONPh$	C_6H_6	AB	47.7	86.4	68.6
25	Me_2N, $PdCl_2$	CH_2Cl_2	AB	48.9	72.4	103.1
26	Me_2N, $PtCl_2$	$CDCl_3$	AB	49.5[c]	52.6[d]	77.8

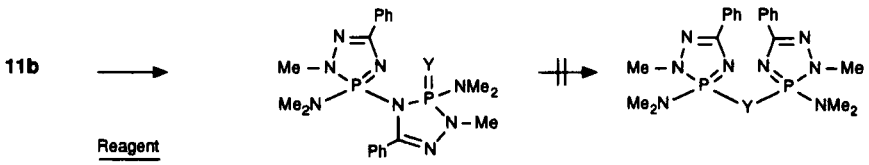
[a] Relative intensity 1.2 : 1.
[b] $^1J_{SeP}$ = 894.8 Hz.
[c] $^2J_{PtP}$ = 145.8 Hz.
[d] $^1J_{PtP}$ = 4946.2 Hz, $\delta^{195}Pt$ = −3429.1.

The tricyclic compounds **5** and **12** can form four isomers, *i.e.* two meso forms (AB_2 spin system) and a *dl* pair (ABC spin system). While a AB_2 type ^{31}P NMR spectrum is found for **5**, ABC type spectra are obtained for **12b,c,d** with rather

similar chemical shifts δ_B and δ_C and with identical coupling constants J_{AB} and J_{AC}. As shown for compound **12c** the B and C signals undergo coalescence around 70°C resulting in an AB_2 spectrum at higher temperature (Fig. 2).

Oxidation

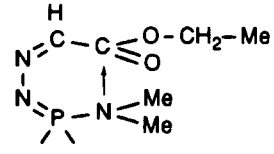
Chemical evidence for structure **11** with one tervalent and one pentavalent phosphorus comes from the oxidation of **11b** by elemental sulfur (equation 10) yielding the sulfide **13**.



Reagent			
S_8	**13**	Y = S	(10)
$(PhPSe_2)_2$	**14**	Y = Se	(11)
PhN_3	**15**	Y = NPh	(12)
$EtO_2C–CHN_2$	**16**	Y = N–N=CH–CO_2Et	(13)

Other selective reaction of the tervalent phosphorus atom are achieved with perselenophosphonic anhydride[9] (equation 11), phenyl azide (equation 12) or ethyl diazoacetate (equation 13). In the ^{31}P NMR spectra the oxidation affects δ_B but not on δ_A; J_{AB} is reduced to approximately half its value (Table II). For none of the products **13–16** the possible rearrangement to the symmetrical isomer was observed (See below, however, the analogous rearrangement of the bromination product).

While the primary addition product of phenyl azide loses dinitrogen to give the iminophosphorane **15**, the adduct **16** of the diazoacetate is stable. The result is a phosphazine[10] in which an intramolecular attractive interaction between the dimethylamino group and the carboxylate group seems feasible.[11]



Such a contact could explain the observed nonequivalence of the two *N*-methyl groups and of the two methylene protons of **16**. At room temperature the methyl groups give rise to two broad proton signals which reach coalescence at approximately 30°C and which on the other hand at −40°C sharpen to two

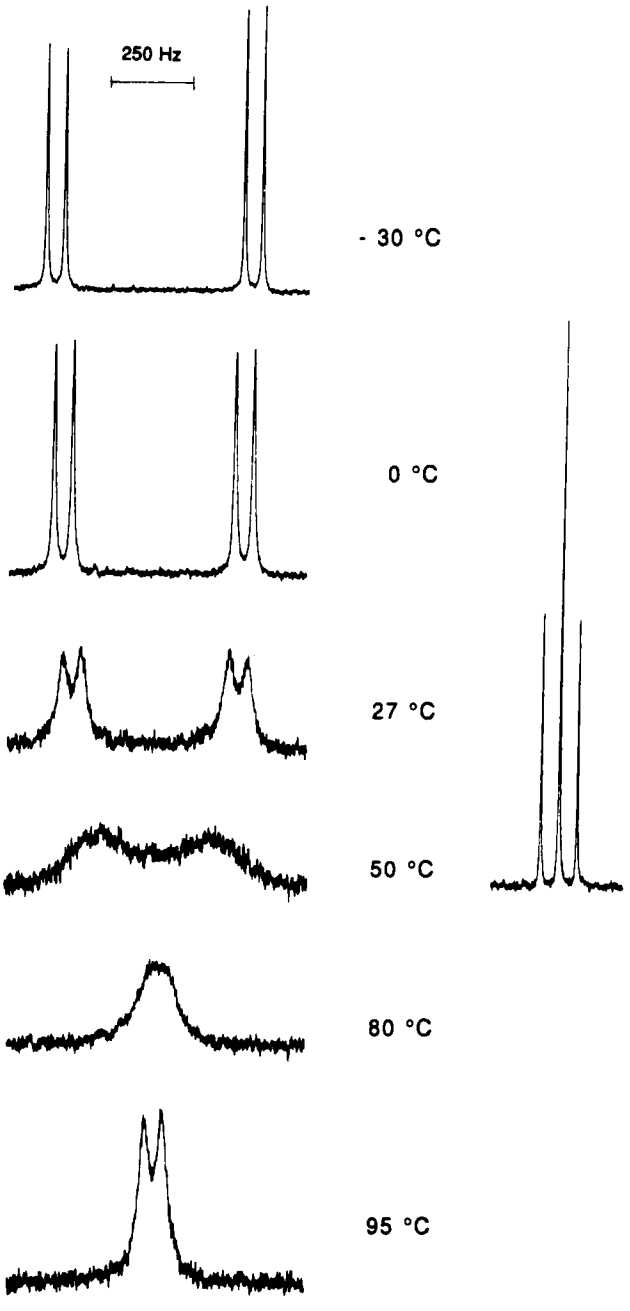
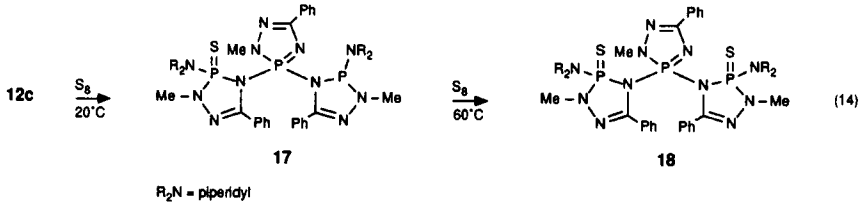


FIGURE 2 ^{31}P NMR Spectra of the tricyclic triazaphole **12c** in toluene-d_8 at different temperatures. Left: $P_{B,C}$ signal(s) of the tervalent phosphorus atoms; right: P_A signal of the pentavalent phosphorus atom which stays the same at all temperatures.

doublets (δ^1H = 2.36 and 2.45, $^3J_{PH}$ = 10.9 and 10.6 Hz). In the room temperature ^{13}C NMR spectrum the methyl groups also give two very broad signals ($\delta^{13}C$ = 35.3 and 38.0). The methylene protons form the AB part of an ABM_3 spin system (δ_A = 4.17, δ_B = 4.25, $\delta_M(CH_3)$ = 1.27, $J_{AB} = {}^2J_{HH}$ = 10.9 Hz, $J_{AM} = J_{BM} = {}^3J_{HH}$ = 7.1 Hz). Another remarkable feature in the ^{13}C NMR spectrum of **16** is the relatively strong coupling of the CH unit ($\delta^{13}C$ = 139.7, $^3J_{PC}$ = 57.1 Hz) to the phosphorus atom.

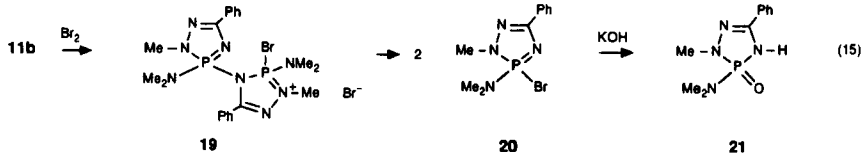
The oxidation of the tricyclic system **12c** with elemental sulfur occurs in two distinct steps (equation 14). At room temperature the reaction stops at the monosulfide **17**. In the ^{31}P NMR spectra the stepwise oxidation is accompanied by a decrease at first of one, then of both coupling constants $^2J_{PP}$ (Table II). For the disulfide **18** as for **12c** the less symmetric isomer is indicated by the ABC spin system in the ^{31}P NMR spectrum.



(14)

Bromine adds to **11b** as expected (equation 15) to give the bromophosphonium bromide **19** (Table II) which spontaneously converts to the monomer **20** (Table I).

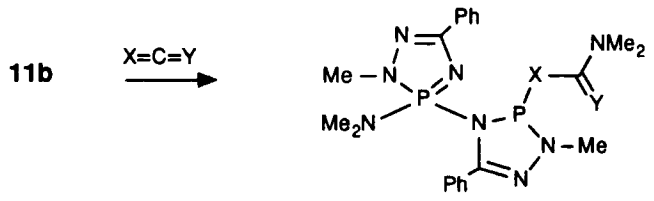
Reaction of the 3-bromo-3-dimethylamino-triazaphosphole **20** with dimethylamine gives the bis(dimethylamino) derivative **10b**, reaction with potassium hydroxide the oxide **21** (Table I).



(15)

Heterocumulene Addition

Electrophilic heterocumulenes can be expected to react selectively with the tervalent phosphorus of **11b**. Carbon disulfide adds loosely and reversibly to **11b** (equation 16). In a 0.2 molar benzene solution at room temperature the adduct **22** is half dissociated and it takes the tenfold molar amount of CS_2 to shift the equilibrium 95% to the adduct side.



X = S, Y = S:	**22**	(16)
X = NPh, Y = S:	**23**	(17)
X = NPh, Y = O:	**24**	(18)

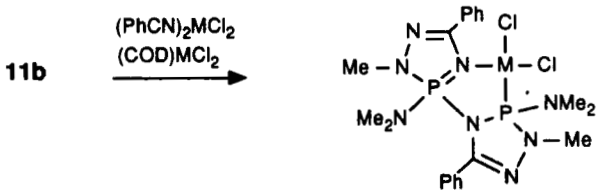
In the adduct the carbon disulfide has inserted into the PN bond at the tervalent phosphorus leading to the dithiocarbamato derivative **22**. The rotation of its dimethylamino group about the CN bond is restricted (obviously by some π-character of this bond): While the two methyl groups give a broad averaged ^{1}H NMR signal at room temperature, the signal separates into two sharp ones (δ = 2.87 and 3.31) at −40°C. They show no coupling to ^{31}P (which was $^3J_{PH}$ = 8.5 Hz in the starting compound **11b**). Indicative for the structure of **22** is furthermore the ^{31}P coupling $^2J_{PC}$ = 19.4 Hz of the carbon atom coming from CS_2.

The insertion of CS_2 into a λ^3PN bond is long known[12–14] and its mechanism has been discussed. For $P(NMe_2)_3$ a threefold insertion is known.[13] In case of **11b** only the exocyclic PN bond is affected, however, not the two endocyclic ones. In a corresponding way phenyl isothiocyanate and phenyl isocyanate insert with their C=N bonds into the λ^3PN bond of **11b** to give the thioureido and ureido derivatives **23** and **24**. The reactions (17, 18) are slower than the formation of **22** and need warming to 60°C for several hours.

Complex Formation

In the reaction with the benzonitrile or cyclooctadiene complex of $PdCl_2$ and $PtCl_2$ **11b** replaces the neutral ligands (equation 19). In the products **25**, **26** the bicyclic triazaphosphole thus occupies two coordination sites at the metal center and acts as chelating ligand.

While the chemical shift of the pentavalent phosphorus atom δ_A of **11b** remains almost unchanged in the complexes **25** and **26**, that of the tervalent phosphorus δ_B moves to higher field in the Pd complex and even more so in the Pt complex (Table II). In case of the platinum compound **26** the structure is further confirmed by the ^{195}Pt^{31}P coupling constants. The coupling of the pentavalent and tervalent phosphorus ($^2J_{PtP}$ = 145.8 Hz and $^1J_{PtP}$ = 4946.2 Hz)

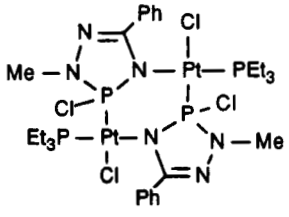


(19)

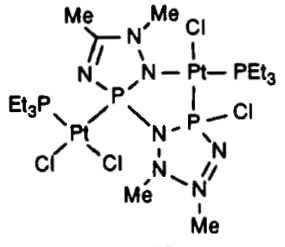
M = Pd **25**
M = Pt **26**

may be compared to the two and one bond coupling constants ($^2J_{PtP}$ = 124 Hz and $^1J_{PtP}$ = 5728 Hz) in the complex **27**[15] from the triazaphosphole **1** and $(Et_3PPtCl_2)_2$.

The coupling constants $^{1,2}J_{PtP}$ are found also in the ^{195}Pt NMR signal. The platinum chemical shift of **26** (Table II) corresponds to that of *cis*-$C_5H_5N(Ph_3P)PtCl_2$ with an alike coordination sphere ($\delta^{195}Pt = -3400$).[16]



27



28

A platinum complex **28**[15] with the chelating combination of two triazaphosphole rings, which consequently strongly resembles complex **26**, has been obtained from the reaction of 1,5-dimethyl-1,2,4,3-triazaphosphole and $(Et_3PPtCl_2)_2$.

EXPERIMENTAL

All manipulations were carried out in flame-dried glassware under argon using the Schlenk technique. Solvents were dried over molecular sieves (4 Å). Melting points were determined in sealed capillaries.

NMR: JEOL GSX 270 (^{31}P, ^{195}Pt), JEOL EX 400 (^1H, ^{13}C) with Me_4Si (int.), 85% H_3PO_4 (ext.) and aqu. Na_2PtCl_6 (ext.) as standards. The ^{31}P NMR data are given in Tables I and II. Most of the products were also confirmed by ^1H and ^{13}C NMR spectra which are mentioned here only in part, however.

11b: 3.94 g (22.0 mmol) **1** and 7.50 g (11.0 mmol) **3** in 120 ml benzene were stirred at room temperature for 1 h yielding a clear solution. Then 7.0 ml (113 mmol) dimethylamine in 10 ml diethylether were added. After 18 h the dimethylammonium bromide was removed, the filtrate evaporated under reduced pressure and the residual yellow oil dissolved in 25 ml acetonitrile. The solution was kept at −20°C and yielded 2.44 mg of (25%) **11b**, mp 123–124°C.

$C_{20}H_{28}N_8P_2$ (442.4) calcd. C 54.29 H 6.38 N 25.33
found C 54.95 H 6.76 N 24.93.

12b: 1.77 g (10.0 mmol) **1** and 3.37 g (5.0 mmol) **3** were dissolved in 40 ml benzene. To the solution which according to the ^{31}P NMR spectrum contained the starting compounds together with **4**, **5** and **6** 1.80 g (40 mmol) of dimethylamine in diethylether were added dropwise. The precipitated dimethylammonium bromide was removed by filtration. Evaporation of the filtrate left a yellow oil which was dissolved in acetonitrile. From this solution crystallized 0.90 g (29%) **12b**, mp 196–197°C.

$C_{28}H_{36}N_{11}P_3$ (619.6) calcd. C 54.28 H 5.86 N 24.87
found C 54.55 H 6.11 N 24.63.

The filtrate, which according to the ^{31}P NMR spectrum contained compound **11b** besides **1** and **10b** was heated to 160°C at 10^{-2} mbar. It distilled completely yielding a mixture of only **1** and **10b**.

12c: To the solution of 386 mg (2.20 mmol) **1** and 734 mg (1.10 mmol) **3** in 15 ml benzene after 30 min 620 µl (4.40 mmol) piperidine in 4 ml benzene was added. After 2 h the solution was filtered, the filtrat evaporated and 15 ml acetonitrile added to the residue. Yield 3.17 mg (29%) of **12c**, mp 159–160°C.

$C_{34}H_{44}N_{11}P_3$ 0.5 C_6H_6 (738.8) calcd. C 60.17 H 6.41 N 20.86
found C 60.21 H 6.67 N 20.59.

13: To the filtrate prepared as for **11b** from 1.77 g (10.0 mmol) **1**, 3.37 g (5.0 mmol) **3** and 1.80 g (40 mmol) Me_2NH 0.32 g (10 mmol) sulfur was added. After heating to reflux for 2d, concentration to 5 ml and filtering, 10 ml of acetonitrile were added. Yield 1.60 g (34%) **13**, mp 188–190°C.

$C_{20}H_{28}N_8P_2S$ (474.5) calcd. C 50.63 H 5.95 N 23.61
found C 50.87 H 5.84 N 23.82.

14: The solution of 140 mg (0.31 mmol) **11b** and 84 mg (0.16 mmol) $Ph_2P_2Se_4$ in 8 ml acetonitrile was filtered after 1 d and kept at −20°C. Yield 56 mg (67%) of **14**, mp 153–155°C.

$C_{20}H_{28}N_8P_2Se$ (521.4) calcd. C 46.07 H 5.41 N 21.49
found C 46.02 H 5.29 N 20.93.

15: The solution of 38 mg (0.08 mmol) **11b** and 10 mg (0.08 mmol) phenyl azide in 0.5 ml chloroform was warmed to 50°C for 18 h. Removal of solvent gave 28 mg (69%) of **15**, mp 107–109°C.

$C_{26}H_{33}N_9P_2$ (533.6) calcd. C 58.53 H 6.23 N 23.63
found C 57.56 H 6.69 N 23.21.

16: The solution of 156 mg (0.35 mmol) **11b** and 37µl (0.35 mmol) ethyl diazoacetate in 15 ml benzene was warmed to 60°C for 4 d. After removal of the solvent the residue was dissolved in 8 ml acetonitrile and kept at −20°C. Yield 195 mg (45%) of **16**, mp 122–123°C.

$C_{24}H_{34}N_{10}P_2O_2$ (556.5) calcd. C 51.80 H 6.16 N 25.17
found C 52.13 H 6.21 N 25.59.

17, 18: To the solution of 34 mg (0.05 mmol) **12c** in 0.5 ml benzene 4 mg (0.12 mmol) elemental sulfur were added. After 3 d at room temperature the ^{31}P NMR spectra showed that formation of **17** was complete and that no further reaction takes place. With warming to 60°C the reaction to **18** was complete after 6 more days.

22: To solutions of 40 mg (0.09 mmol) **11b** in 0.5 ml benzene different amounts of CS_2 were added. In every case the ^{31}P NMR spectra showed the signals of **11b** together with those of the adduct **22** (Table II). With an increasing molar ratio of CS_2/**11b** the resulting share of **22** relative to the sum of **11b** and **22** also increased:

0.5 0.9 1.4 2.0 5 10 equivalents CS_2 added
28 48 60 69 90 95 molar % **22**

25: The solutions of 245 mg (0.86 mmol) dichloro(1,2:5,6-cyclooctadiene)palladium in 5 ml dichloromethane and of 380 mg (0.86 mmol) **11b** in 3 ml dichloromethane were combined. After reducing the volume to 4 ml **25** separated. Yield 283 mg (53%) of **25**, mp 160°C (decomp.).

$C_{20}H_{28}Cl_2N_8P_2Pd$ (619.7) calcd. C 38.76 H 4.55 N 18.08
found C 38.45 H 4.59 N 17.81.

The same product was obtained from bis(benzonitrile)dichloropalladium.

26: As before from 312 mg (0.66 mmol) bis(benzonitrile)dichloroplatinum and 292 mg (0.66 mmol) **11b**. Yield 158 mg (30%) of **26** as light yellow powder, mp 255°C (decomp.).

$C_{20}H_{28}Cl_2N_8P_2Pt$ (708.4) calcd. C 33.91 H 3.98 N 15.82
found C 33.70 H 4.00 N 15.62.

The same product was obtained from dichloro(1,2:5,6-cyclooctadiene)platinum.

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