2,4-Diphosphoranediyl-1,3-diphosphetanes

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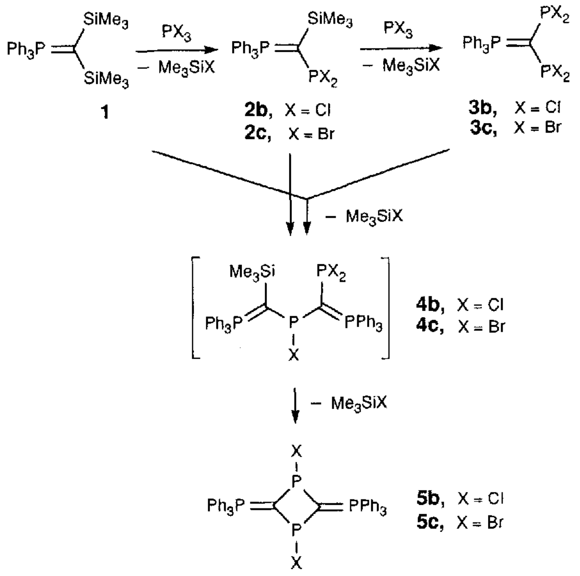
The 1,3-dichloro- and 1,3-dibromo-substituted title compounds **5b**, **c** result from the condensation of triphenylphosphonium-bis(trimethylsilyl)methylide **1** with PCl_3 and PBr_3. The chloro derivative **5b** undergoes a variety of single and double substitution reactions, of which some have merely been tested and others have been made preparative use of. The substitution of one chloride by an ylidyl, amino, phosphino, or metal carbonyl group is accompanied by the spontaneous dissociation of the other P−Cl bond to yield the 1,3-diphosphetenium chlorides **14**/**15**, **19**, **31** and **36**, respectively. In other cases (**9**, **27**, **32**) dissociation can be achieved by means of a Lewis acid. Protonation of **5b** occurs at the carbon ring members; methylation and formation of transition metal complexes occurs at a phosphorus ring member. PCl_3 degrades the four-membered ring of **5b** or enlarges the ring to yield 3,5-diphosphoranediyl-1,2,4-triphospholane derivatives **39**, **40**, **42**.

The alternating combination of the divalent units Ph_3PC and PX (X = Cl, Br) leads to a new class of oligomers, $(Ph_3PCPX)_n$ (n = 2, 3, 4)[1−4]. The characteristic feature of these compounds is the easy dissociation of the PX bonds, with the tendency towards ionic structures increasing with increasing n. The four-membered cyclic dimers, 1,3-dihalo-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetanes are not dissociated. As will be shown here, however, their substitution may be accompanied by dissociation.

Halogensubstituted 1,3-Diphosphetanes

The bis(trimethylsilyl)ylide **1** reacts with phosphorus trichloride and tribromide in two separate steps to give the dihalophosphino (trimethylsilyl)ylides **2** and the bis(dihalophosphino)ylides **3**[5,6]. The chlorosubstituted diphosphetane **5b** results from the slow self-condensation of **2b**[1,3]. To obtain the bromosubstituted diphosphetane **5c**, the bis(trimethylsilyl)ylide **1** is condensed with **3c**[3].

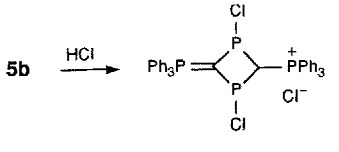
The latter reaction necessarily passes through an intermediate of type **4**, and although the reaction leading from **2b** to **5b** might instead involve an intramolecular elimination of Me_3SiCl from **2b** and the dimerization of the resulting intermediate, it seems more likely that this reaction also proceeds by an intermolecular condensation and thus also passes through an intermediate of type **4**.



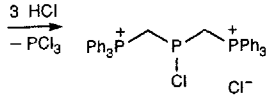
An X-ray structure analysis of **5b**[3] shows an almost planar arrangement of the four ring members and the two exocyclic phosphorus atoms. The two P−Cl bonds are cis to each other[7] and virtually eclipsed to the filled p_z orbitals at the ylidic carbon atoms, with Cl−P−C−P dihedral angles of 82 and 69° for one chlorine atom and 83 and 70° for the other. This conformation favors charge transfer to the antibonding orbitals of the P−Cl bonds (negative hyperconjugation[8−11]) and results in extremely long P−Cl bonds, of 220.4(4) and 225.1(3) pm[12] as compared to 204 pm in PCl_3.

The chemical behaviour of **5b** has been characterized by a variety of reactions. The reactions were followed and the products were identified by their ^{31}P-NMR spectra. The data are compiled in Tables 1−3. The products were isolated from only some of the reactions.

5b readily takes on hydrogen chloride − even unintentionally from dichloromethane used as a solvent − to give the hydrochloride **6b**. The analogous bromo compound **6c** has also been observed. With more HCl one of the phosphorus ring members is lost as PCl_3. The resulting acyclic dicationic chlorophosphine **7** is known as the adduct of two equivalents of triphenylphosphonium methylide with one of PCl_3[13]. Its formation from **5b** probably follows a pathway similar to that discussed for the reaction of **5b** with methanol (see below). It involves the opening of P–C bonds under the nucleophilic attack of chloride ions. If this attack is prevented by complexing the chloride ions with $AlCl_3$, the dication is conserved as tetrachloroaluminate **8**.



6b



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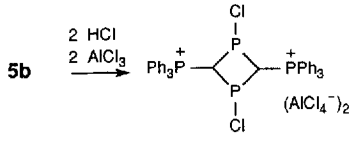

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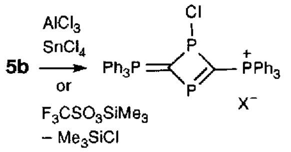
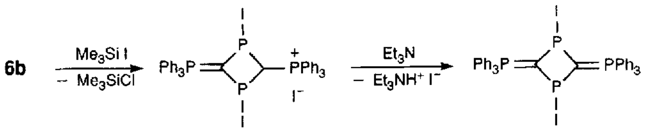
In the absence of HCl aluminum chloride abstracts a chloride ion from **5b** and gives (among other products) the 1-chloro-1,3-diphosphetenium tetrachloroaluminate **9a**[2]. Tin tetrachloride similarly gives **9b**.



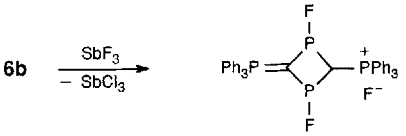
9a, X = $AlCl_4$
9b, X = $SnCl_5$
9c, X = F_3CSO_3

With three moles of trimethyliodosilane the PCl units of **6b** are converted to PI units, yielding the hydroiodide **6d** from which the 1,3-diiododiphosphetane **5d** can be freed with triethylamine.



6d **5d**

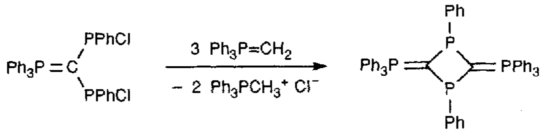
With one mole of antimony trifluoride the PCl units of **6b** are converted to PF units, yielding the hydrofluoride **6a** of the 1,3-difluorodiphosphetane. Attempts to deprotonate **6a** with triethylamine failed due to decomposition reactions.



6a

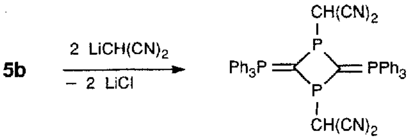
Organosubstituted 1,3-Diphosphetanes

1,3-Organosubstituted 2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetanes are accessible either by direct synthesis or by substitution reactions from **5b**. As an example of the first route, the 1,3-diphenyl derivative **11** was prepared from the bis(chlorophenylphosphino)ylide **10** and three moles of the triphenylphosphonium methylide in a double substitution and transylidation reaction.



10 **11**

The preparation of the 1,3-bis(dicyanomethyl) derivative **12** by reaction of **5b** with lithiomalodinitrile provides an example of the second route. The singly substituted product is not observed in the course of this reaction; if the reactants are used in a 1:1 molar ratio, half of **5b** is converted to **12** and the other half is left unchanged. It seems that the substitution at P-1 enhances the substitution rate at P-3. With regard to those ylidylphosphorus chalcogenides which may be stable as monomers[14], in **12** a 1,3-proton shift and subsequent monomerization to give a push-pull substituted phosphaethene **13** seemed possible but was not observed at room temperature.



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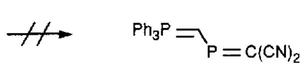

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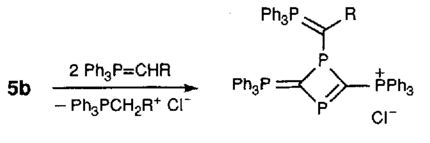
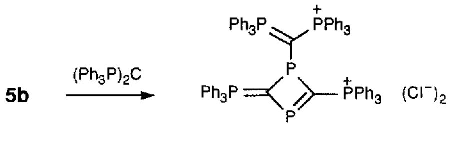
The reaction of **5b** with the triphenylphosphonium ylides $Ph_3P{=}CHR$ (R = Me, Et) proceeds in a 1:2 molar ratio and yields the ionic monosubstitution products **14a**, **b**, which thus represent examples of the spontaneous dissociation mentioned in the Introduction. Although in the symmetric starting compound **5b** the two phosphorus ring members participate equally in the electron transfer from the ylide carbon atoms (see the discussion of its structure), here the ylide substituted ring member P-1 will participate less and therefore will leave a greater share to P-3. This renders the nature of the P–Cl bond at P-3 much the same as that in other known cyclic or acyclic bis(phosphoranediyl)chlorophosphines, which all undergo spontaneous dissociation[1,15–17].



14a, R = Me
14b, R = Et

For the same reason the addition of hexaphenyl carbodiphosphorane to **5b** leads to the dissociated product **15** with a doubly charged cation[1].



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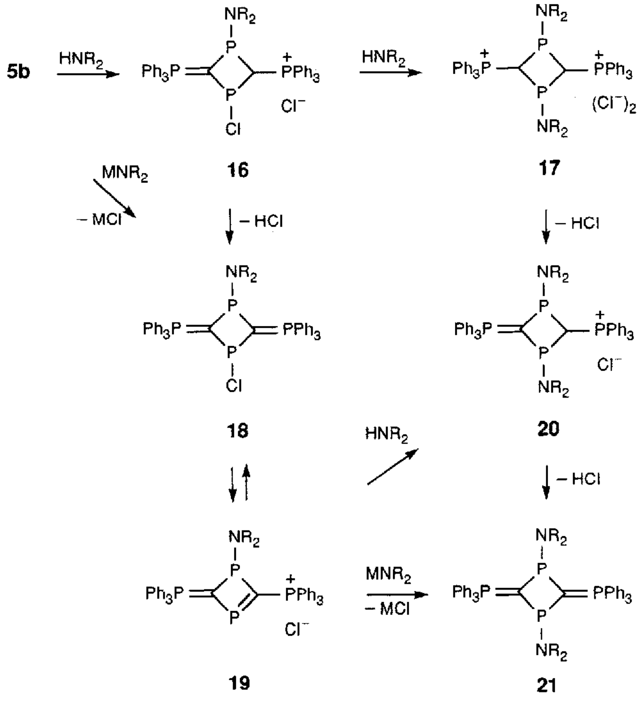
Reactions of the Dichloro-1,3-diphoshetane with Amines

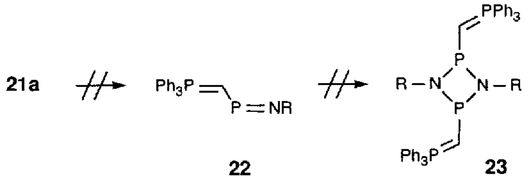
Compound **5b** combines the possibility of nucleophilic substitution at the PCl units with the basicity of the ylide moieties. The reactions with protic nucleophiles (such as non-tertiary amines) that can be anticipated from this situation are summarized in Scheme 1. Two equivalents of a non-tertiary amine may add in steps to yield the diphosphonio-1,3-diphosphetane chlorides **16** and **17**[18]. Their deprotonation may then give the substitution products **18** and **20** with a possibility of the monosubstituted product **18** dissociating to yield its ionic form **19**[1]. Direct access to the substitution products **18/19** and **21** can be expected from reaction of **5b** with trimethylsilylamines or lithium amides MNR$_2$ (M = Me$_3$Si, Li).

Scheme 1

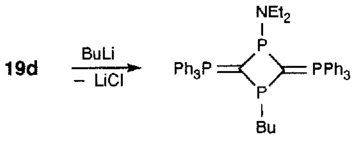


The examples investigated verify all the anticipated possibilities. Thus aniline and cyclohexylamine add in two steps to **5b** to yield the 2,4-bis(triphenylphosphonio)-1,3-diphosphetane dichlorides **17a** (R$_2$ = H, Ph) and **17b** (R$_2$ = H, C$_6$H$_{11}$). **17a** is deprotonated once by triethylamine to give **20a** (R$_2$ = H, Ph), but not a second time to reach **21a**. One equivalent of diethylamine or morpholine adds to **5b** to give **16d** (R$_2$ = Et$_2$) or **16e** (R$_2$ = C$_4$H$_8$O), respectively; with two equivalents of these amines compounds **19d**, **e** are formed, and these add a third equivalent to give **20d**, **e**. Neither **20d** nor **20e** is further deprotonated by triethylamine.

Substitution of a chlorine atom in **5b** with trimethylsilylamines and -imines Me$_3$SiNR$_2$ (R$_2$ = Me$_2$, Et$_2$, C$_4$H$_8$O, CPh$_2$) yield the ionic products **19c** (R$_2$ = Me$_2$), **19d** (R$_2$ = Et$_2$), **19e** (R$_2$ = C$_4$H$_8$O) and **19f** (R$_2$ = CPh$_2$). As with compounds **14** and **15**, the substitution at P-1 is again accompanied by dissociation at P-3. An excess of the trimethylsilylamine does not alter the product. However, disubstituted products **21a** (R$_2$ = H, Ph) and **21b** (R$_2$ = H, C$_6$H$_{11}$) are obtained from **5b** with two equivalents of the respective lithium amides. Like for compound **12**, no 1,3-proton shift was observed for **21a** or **21b** either. Such a shift could have led to the iminophosphanes **22** or to the diazadiphosphetidines **23** as their dimers.



21d (R$_2$ = Et$_2$) is obtained from **19d** by the addition of one equivalent of lithium diethylamide. Butyllithium adds analogously to give the unsymmetric diphosphetane **24**.



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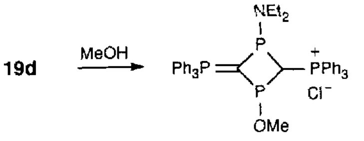
On protonation of **19d** with HBF$_4$ the chloride ion reassociates to give **16d** with BF$_4^-$ in place of Cl$^-$. Methanol adds to **19d**, yielding the mixed substituted product **25**. Oxidation of **19d** with selenium also causes reassociation of the chloride ion[2]. From the product **26** the latter can be abstracted again with AlCl$_3$ to give **27**.

Reaction of the Dichloro-1,3-diphosphetane with Methanol

The reaction of **5b** with methanol (as that with HCl, see above) leads to a degradation of the 1,3-diphosphetane ring. Trimethyl phosphite and methoxybis(triphenylphos-



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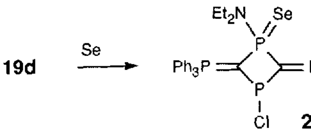

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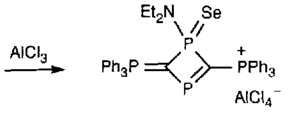

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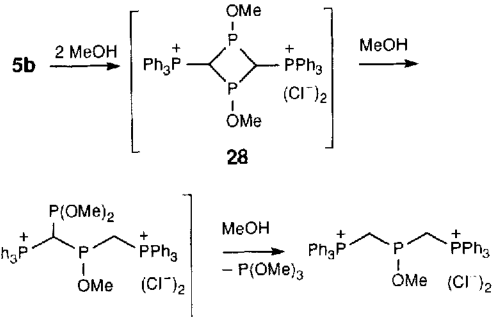
phoniomethyl)phosphane dichloride **30** are identified as products.



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29

30

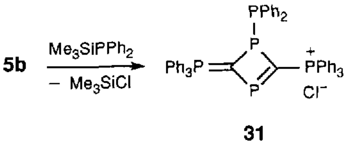
This, at first unexpected, unsymmetrical ring cleavage can be understood by following a pathway initially analogous to that of Scheme 1: The addition of two moles of alcohol should result in a doubly ionic intermediate **28** (equivalent to **17**, with OMe in place of NR_2). The ring of **28** may then open under the nucleophilic attack of a third equivalent of alcohol to give the intermediate **29**. If its terminal $P(OMe)_2$ group is easier attacked than its central POMe group, the alcoholysis of a second P–C bond will consequently lead to **30** as the final product. The use of just two equivalents of methanol does not stop the reaction at the stage of the intermediate, but instead leaves half of the **5b** unreacted.

Reactions of the Dichloro-1,3-diphosphetane with Phosphanes

The condensation of **5b** with diphenyl(trimethylsilyl)-phosphane, like that with trimethylsilylamines, yields an ionic product **31**. No reaction of **5b** with triphenylphosphine is observed. However, with additional aluminium chloride the doubly charged cation in **32** is formed[2,3].

Methylation of the Dichloro-1,3-diphosphetane

While **5b** is protonated at the carbon ring members (see above), it is alkylated by methyl iodide or dimethyl sulfate at a phosphorus ring member to yield **33a** and **33b**, respectively. The isomeric *C*-methylated cation and the corresponding ethyl derivative can be achieved, however, by direct synthesis in the form of their chlorides **34a**, **b**. Isomerization was not observed for either **33** or **34**, nor could it be thermally induced.



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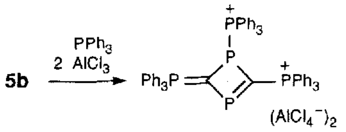

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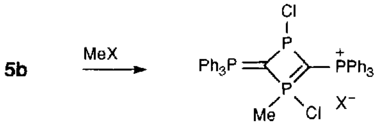
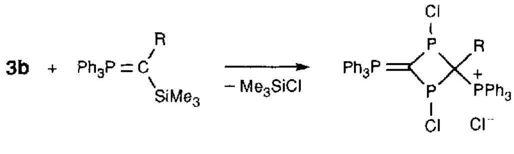


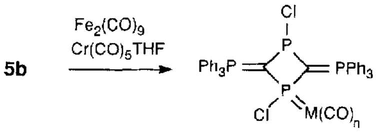
33a, X = I
33b, X = $MeSO_4$



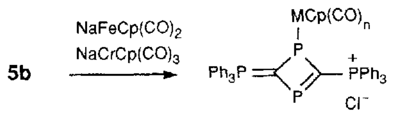
34a, R = Me
34b, R = Et

Reactions of the Dichloro-1,3-diphosphetane with Metal Carbonyls and Carbonylates

In accord with the methylation, 16e-metalcarbonyl fragments also add to a phosphorus ring member of **5b** to give the complexes **35a**, **b**. With metal carbonylates **5b** undergoes a substitution reaction and, as in case of the ylidyl, amino, and phosphino derivatives, the products **36** prove to be ionic.



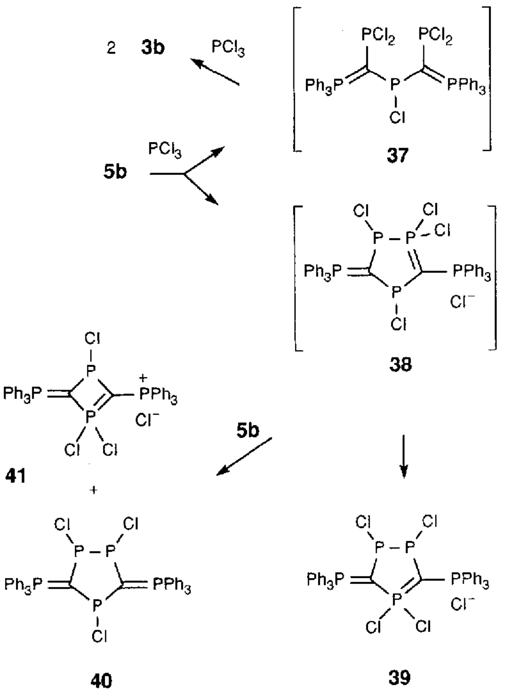
35a, $M(CO)_n$ = $Fe(CO)_4$
35b, $M(CO)_n$ = $Cr(CO)_5$



36a, $MCp(CO)_n$ = $FeCp(CO)_2$
36b, $MCp(CO)_n$ = $CrCp(CO)_3$

Reactions of the Chloro-1,2-diphosphetane with Phosphorus Trichloride

Reaction of **5b** and PCl_3 in different molar ratios always gives a mixture of products. These can be understood as resulting from electrophilic attack of PCl_3 on either a carbon or a phosphorus ring member, yielding the isomeric (and possibly tautomeric) adducts **37** and **38**, which are, however, not observed (Scheme 2). The addition of a second molecule of PCl_3 to **37** then leads back to **3b**. This extent of this reaction is reduced when less PCl_3 is available, and it can be completely avoided by lowering the temperature. Intermediate **38** on the other hand undergoes either an intramolecular redox reaction to yield 1,2,4,4-tetrachloro-1,2,4-triphospholanium chloride (**39**) or a reaction with a second molecule of **5b** to yield 1,2,4-trichloro-1,2,4-triphospholane (**40**) as the reduced part and 1,3,3-trichloro-1,3-diphosphetanium chloride (**41**) as the oxidized part. The latter two compounds are generally the major products and are found in nearly equimolar amounts, thus indicating that they originate from the same reaction step.

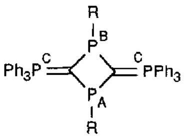


If the reaction of **5b** and PCl_3 is carried out in the presence of tin dichloride, **40** is further reduced to the 1,2,4-triphosphole salt **42**, and the second half of **5b** is transformed to the diphosphetenium salt **9b** and is thus protected from further electrophilic attack. The synthesis and chemistry of the bis(triphenylphosphonio)-1,2,4-triphospholide ion, such as in **42**, have been described in a preceding paper[17].

^{31}P-NMR Spectra

The ^{31}P-NMR data of all observed compounds are compiled in Tables 1–3. The symmetry of the dihalodiphosphetanes **5** is reflected by their ^{31}P-NMR spectra, of A_2C_2 spin type (see Table 1; A for the ring phosphorus atoms, C for the exocyclic phosphorus atoms). The dissociation of a P–Cl bond, the unlike substitution of the two ring phos-

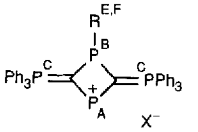
Table 1. ^{31}P-NMR data of 2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetanes **5**, **11**, **12**, **21** (A_2C_2 spin systems) and **24**, **26**, **35** (ABC_2 spin systems) and of 2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetanium salts **33**, **41** (ABC_2 spin systems), in CH_2Cl_2 if not otherwise indicated; coupling constants *J* in Hz



	R(P_A)	R(P_B)	δ_A	δ_B	δ_C	$^2J_{AB}$	$^2J_{AC}$	$^2J_{BC}$
5b	Cl	Cl	194.6		16.5		51.9	
5b[a]	Cl	Cl	189.5		16.0		51.9	
5b[b]	Cl	Cl	186.3		16.2		48.3	
5c	Br	Br	214.7		15.5		48.1	
5d	I	I	230.6		15.6		44.3	
11[c]	Ph	Ph	72.0		14.4		96.6	
12	$CH(CN)_2$	$CH(CN)_2$	-23.5		26.5		61.1	
21a[c]	PhNH	PhNH	73.1		14.4		91.6	
21b	$C_6H_{11}NH$	$C_6H_{11}NH$	65.0		10.5		95.7	
21d	Et_2N	Et_2N	61.7		10.0		104.1	
24	Bu	Et_2N	105.6	81.0	10.8	93.6	105.8	89.5
26	Cl	Et_2N, Se[d]	216.0	45.0	10.8	34.6	67.2	16.3
33a	Cl	Cl, Me^+ I^-	151.2	48.2	14.9	85.5	42.7	12.2
33b	Cl	Cl, Me^+ $MeSO_4^-$	150.3	48.8	15.1	89.5	42.8	12.2
35a[c]	Cl	Cl, $Fe(CO)_4$	177.4	167,5	16.1	109.4	57.0	20.3
35b	Cl	Cl, $Cr(CO)_5$	172.6	165.6	15.2	139.6	46.5	19.9
41	Cl	Cl_2^+ Cl^-	121.6	8.4	10.9	35.1	41.2	13.1

[a] In C_6H_5Cl. – [b] In C_6H_6. – [c] In THF. – [d] $^1J_{SeP}$ = 710.0.

Table 2. ^{31}P-NMR data of 2,4-bis(triphenylphosphoranediyl-1,3-diphosphetenium salts **9**, **19**, **27**, **36** (ABC$_2$ spin systems), **14**, **31**, **32** (ABC$_2$E spin systems) and **15** (ABC$_2$EF spin system), in CH$_2$Cl$_2$ if not otherwise indicated; coupling constants J in Hz



	R	X	δ_A	δ_B	δ_C	$\delta_{E,F}$	$^2J_{AB}$	$^2J_{AC}$	$^2J_{BC}$	$^{1,2}J_{BE,F}$	$^3J_{AE}$
9a	Cl	AlCl$_4$	407.8	76.0	19.4		122.1	50.7	32.6		
9b	Cl	SnCl$_5$	409.5	75.9	17.9		120.9	48.3	32.9		
9c	Cl	TfO	413.5	75.8	17.1		117.9	44.7	34.0		
14a	Ph$_3$P=CMe	Cl	350.8	48.4	16.0	22.2	98.6	56.0	23.4	192.3	
14b	Ph$_3$P=CEt	Cl	343.8	45.0	16.0	22.1	105.8	57.0	24.9	206.5	
15	(Ph$_3$P)$_2$C$^+$ Cl$^-$	Cl	370.1	0.0	17.3	24.5	119.6	65.1	26.1	179.8	
						24.6				16.8[a]	
19c	Me$_2$N	Cl	372.5	64.2	14.4		97.6	46.8	32.6		
19d	Et$_2$N	Cl	372.2	57.5	14.5		99.7	49.3	32.1		
27	Et$_2$N, Se^b	AlCl$_4$	429.5	44.0	14.9		38.7	46.8	< 3		
19e[c]	OC$_4$H$_8$N	Cl	379.1	60.7	14.2		97.6	48.8	32.5		
19f	Ph$_2$C=N	Cl	266.7	84.3	14.2		135.3	57.0	39.2		
31	Ph$_2$P	Cl	403.5	60.6	17.5	-1,4	81.4	52.9	24.5	270.6	26.4
32	Ph$_3$P$^+$ AlCl$_4^-$	AlCl$_4$	441.7	21.1	19.7	1.7	91.6	54.9	22.4	444.6	39.4
36a[c]	CpFe(CO)$_2$	Cl	366.8	100.8	19.9		120.1	57.0	18.4		
36b	CpCr(CO)$_3$	Cl	381.3	55.7	17.2		124.1	57.0	20.3		

[a] $^2J_{EF}$ = 54.7. – [b] $^1J_{SeP}$ = 562.6. – [c] In THF.

phorus atoms, the alkylation or complexation of one of them, and/or the protonation of one of the ring carbon atoms lowers this symmetry to the spin systems indicated in the Table captions. The chemical shifts of the phosphorus ring members clearly indicate their coordination number and the nature of their substituents. Signals at very low field, i.e. between δ = 442 and δ = 267, are a sign of two-coordinate (phosphenium-type) phosphorus atoms. This range is followed by the ranges of halo- and amino-substituted three-coordinate phosphorus atoms (δ = 231–76 and δ = 88–7, respectively). The signals of the triphenylphosphoranediyl and triphenylphosphonio groups are found in the narrow range δ = 30–10; where they are both present in the same ion, as in compounds **6** and **34**, the signal of the charged group is generally found at lower field.

The two Ph$_3$P groups in compound **15**, which were introduced by the addition of a carbodiphosphorane, are not equivalent (signals E and F, Table 2), indicating their fixed endo- and exocyclic orientations. This originates from the pyramidal coordination of the phosphorus ring member and the hindered rotation of its exocyclic P–C bond[19]. The signal with the much larger coupling constant $^2J_{PP}$ is assigned to the exo position, which is synperiplanar to the electron lone pair at P(III).

Experimental Section

All operations were carried out in flame-dried glassware under dry argon using Schlenk techniques. Tetrahydrofuran was dried by reflux with sodium/benzophenone and distillation. Pentane was dried over molecular sieve (4 Å). Dry dichloromethane and benzene were used as obtained (Fluka). Melting points were measured in sealed capillaries and are uncorrected. – NMR: JEOL GSX 270 (^{31}P), JEOL EX 400 (^{1}H, ^{13}C) with Me$_4$Si (int.) and 85% H$_3$PO$_4$ (ext.) as standards. The synthesis of **5b** and **5c** has been described previously[3].

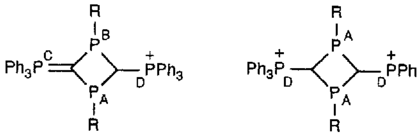
1,3-Dichloro-2-triphenylphosphoranediyl-4-triphenylphosphonio-1,3-diphosphetane Chloride (**6b**): To a solution of 71 mg (0.1 mmol) of **5b** in 0.5 ml of dichloromethane at –78°C, 0.1 ml (0.1 mmol) HCl (1 M in diethyl ether) was added by a syringe. The ^{31}P-NMR spectrum showed the signals of **6b** and **7**. To this solution 0.3 ml (0.3 mmol) of HCl was added. – ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ = 70.4 (t), 23.7 [d, $^2J_{PP}$ = 50.3 Hz (7[13])], 219.3 (PCl$_3$).

1-Chloro-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Tetrachloroaluminate (**9a**): To a solution of 65 mg (0.1 mmol) of **5b** in 0.5 ml of dichloromethane at –78°C, 20 mg (0.1 mmol) of AlCl$_3$ was added. The ^{31}P-NMR spectrum showed mainly the signals of **9a** and **8**.

1-Chloro-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Triflate (**9c**): To a solution of 55 mg (0.1 mmol) of **5b** in 0.5 ml of dichloromethane at –78°C, 22 mg (0.1 mmol) of trimethylsilyltriflate was added. The ^{31}P-NMR spectrum showed the signals of **9c** and **6b**.

1,3-Diiodo-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane (**5d**) *and 1,3-Diiodo-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Iodide* (**6d**): To a solution of 0.43 g (0.63 mmol) of **5b** in 12 ml of dichloromethane at –78°C, 0.38 g (1.95 mmol) of trimethyliodosilane in 3 ml of dichloromethane was added dropwise. The intially yellow solution turned orange and an orange precipitate was formed. After warming to room temperature the precipitate was filtered off and the orange solution was concentrated to half its original volume. The ^{31}P-NMR spectrum showed the signals of **6d**. After adding 0.09 mg (0.95 mmol) of triethylamine, **5d** separated as an orange precipitate. – Yield 320 mg (54%), m.p. 105–110°C (decomp.). **5d** is almost insoluble in all usual solvents. Its ^{31}P-NMR spectrum was observed from the fil-

Table 3. ^{31}P-NMR data of 2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane ions of **6**, **20**, **34** (A_2CD spin systems) and **16**, **25** (ABCD spin systems) and 2,4-bis(triphenylphosphonio)-1,3-diphosphetane ions of **8**, **17** (A_2D_2 spin systems) in CH_2Cl_2; coupling constants J in Hz



	R(P_A)	R(P_B)	δ_A	δ_B	δ_C	δ_D	$^2J_{AB}$	$^2J_{AC}$	$^2J_{AD}$	$^2J_{BC}$	$^2J_{BD}$	$^4J_{CD}$
6a	F	F	166.9		19.3	22.3		45.8	73.2			19.8
6b	Cl	Cl	153.6		21.0	22.4		55.2	50.6			13.8
6c	Br	Br	162.9		19.7	23.5		50.4	48.9			13.7
6d	I	I	169.8		19.6	24.8		45.7	51.8			10.7
34a[a]	Cl	Cl	177.8		19.4	29.6		52.9	61.9			14.2
34b[b]	Cl	Cl	177.7		19.3	28.4		50.9	59.0			14.2
16b	Cl	$C_6H_{11}NH$	157.3	85.9	21.1	22.1	91.5	71.2	57.0	67.1	46.8	20.3
16c	Cl	Me_2N	155.9	88.0	21.1	22.2	92.6	73.3	54.9	67.1	48.8	18.3
16d	Cl	Et_2N	156.8	85.7	20.6	22.1	95.6	75.2	59.0	67.1	50.9	20.3
16e	Cl	OC_4H_8N	157.5	85.9	20.9	22.1	93.6	71.2	59.0	69.2	48.8	19.3
16f	Cl	$Ph_2C=N$	182.6	85.2	19.4	21.2	91.6	61.0	59.0	45.5	45.6	12.2
20a	PhNH	PhNH	50.7		18.7	21.9		81.4	59.0			24.5
20d	Et_2N	Et_2N	51.7		18.2	23.1		105.8	61.0			32.6
20e	OC_4H_8N	OC_4H_8N	54.7		17.1	22.7		99.7	61.0			28.8
25	OMe	Et_2N	129.5	73.0	19.5	21.3	72.3	85.5	57.0	81.4	54.9	23.4
8	Cl		83.2			24.7			61.0			
[c]	^{t}Bu		21.4			21.4						
17a	PhNH		6.7			22.9			67.2			
17b	$C_6H_{11}NH$		7.1			25.1			67.2			

[a] Me in place of H. – [b] Et in place of H. – [c] Ref.[17].

trate. – $C_{38}H_{30}P_4I_2 \cdot CH_2Cl_2$ (949.29): calcd. C 49.35, H 3.40; found C 49.55, H 3.82.

1,3-Difluoro-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Fluoride (**6a**): 0.40 g (0.57 mmol) of **5b** and 0.1 g (0.59 mmol) of SbF_3 were dissolved in a mixture of 5 ml of tetrahydrofuran and 2 ml of dichloromethane. At room temperature the initially yellow solution slowly turned orange. the ^{31}P-NMR spectrum showed the signals of **6a** as the main product (85%).

1,3-Diphenyl-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane (**11**): To a solution of 0.73 g (1.30 mmol) of **10** in 20 ml of tetrahydrofuran at room temperature, 1.08 g (3.91 mmol) of $Ph_3P=CH_2$ in 10 ml of tetrahydrofuran was added dropwise. After stirring for 18 h the formed precipitate was filtered off and identified as methyltriphenylphosphonium chloride by NMR spectroscopy (δ = 22.5). From the concentrated filtrate **11** separated after 18 h as an orange-red precipitate.

1,3-Bis(dicyanomethyl)-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane (**12**): To a suspension of 0.45 g (0.66 mmol) of **5b** in 3 ml of tetrahydrofuran at 0°C, a tetrahydrofuran solution of $LiCH(CN)_2$ from 0.09 g (1.33 mmol) of $CH_2(CN)_2$ and 0.83 ml (1.33 mmol) of *n*-butyllithium (1.6 M in hexane) was added dropwise. After warming to room temperature the beige-coloured precipitate of **12** was filtered off and identified by its ^{31}P-NMR spectrum (40% yield, not pure).

1-(1-Triphenylphosphoranediylethyl)-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**14a**): To a suspension of 0.90 g (1.32 mmol) of **5b** in 7 ml of tetrahydrofuran, a solution of 0.77 g (2.65 mmol) of $Ph_3P=CHMe$ in 3 ml of tetrahydrofuran was added dropwise. After stirring at room temperature the precipitate formed was separated and identified by ^{31}P-NMR spectroscopy as a mixture of **14a** and ethyltriphenylphosphonium chloride. Recrystallization from dichloromethane/pentane gave pure **14a** as the second fraction. – Yield 385 mg (28%), m.p. 165°C (decomp.) – ^{1}H NMR (CD_2Cl_2), 1-substituent: δ = 1.75 (dd, $^3J_{PH}$ = 3.9, 14.7 Hz, 3H, Me), 7.53 (m, 6H, *o*-H), 7.43 (m, 6H, *m*-H), 7.75 (m, 3H, *p*-H); 2,4-substituents: δ = 7.59 (m, 12H, *m*-H), 7.82 (m, 18H, *o*-, *p*-H). – $C_{58}H_{48}ClP_5 \cdot 0.5\ CH_2Cl_2$ (977.81): calcd. C 71.18, H 5.05; found C 71.53, H 5.32.

1-(1-Triphenylphosphoranediylpropyl)-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**14b**): To a suspension of 0.73 g (1.18 mmol) of **5b** in 7 ml of tetrahydrofuran, 0.72 g (2.36 mmol) of $Ph_3P=CHEt$ in 5 ml of tetrahydrofuran was added dropwise. According to its ^{31}P-NMR spectrum the precipitate was a mixture of propyltriphenylphosphonium chloride (δ = 24.9) and **14b**.

1-(1-Triphenylphosphoranediyltriphenylphosphoniomethyl)-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Dichloride (**15**): To a suspension of 0.34 g (0.5 mmol) of **5b** in 5 ml of dichloromethane at 0°C, 0.34 g (0.6 mmol) of $(Ph_3P)_2C$ in 5 ml of dichloromethane was added dropwise. The ^{31}P-NMR spectrum of the solution showed the signals of **15b** together with that of $(Ph_3P)_2CH^+$ ($\delta = 21.1$).

1,3-Bis(anilino)-2,4-bis(triphenylphosphonio)-1,3-diphosphetane Dichloride (**17a**) and *1,3-Bis(anilino)-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Chloride* (**20a**): To a solution of 62 mg (0.18 mmol) of **5b** in 0.5 ml of dichloromethane, 17 mg (0.18 mmol) of aniline was added. The ^{31}P-NMR spectrum showed the signals of **17a** and after adding 43 mg (0.43 mmol) of triethylamine those of **20a** as the main product.

1,3-Bis(anilino)-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane (**21a**): To a solution of 20 mg (0.21 mmol) of aniline in 2 ml of tetrahydrofuran at 0°C, 0.14 ml (0.21 mmol) of a 1.6 M solution of *n*-BuLi in hexane was added. After stirring for 30 min this solution was added dropwise to a suspension of 72 mg (0.11 mmol) of **5b** in 5 ml of tetrahydrofuran. After 3 h the solution was filtered and concentrated in vacuo. Its ^{31}P-NMR spectrum showed the signals of **21a** as the main product.

1,3-Bis(cyclohexylamino)-2,4-bis(triphenylphosphonio)-1,3-diphosphetane Dichloride (**17b**): To a solution of 51 mg (0.08 mmol) of **5b** in dichloromethane, 14 mg (0.15 mmol) of cyclohexylamine was added. Its ^{31}P-NMR spectrum showed the signals of **17b**.

1,3-Bis(cyclohexylamino)-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane (**21b**) and *1-Cyclohexylamino-3-chloro-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Chloride* (**16b**): To a solution of 0.26 g (2.6 mmol) of cyclohexylamine in 10 ml of tetrahydrofuran at 0°C, 1.59 ml (2.6 mmol) of a 1.6 M solution of *n*-BuLi in hexane was added. After stirring for 30 min the resulting red solution was added dropwise at 0°C to a suspension of 0.90 g (1.30 mmol) of **5b** in 6 ml of tetrahydrofuran. After stirring for 20 h all volatiles were removed in vacuo. The ^{31}P-NMR spectrum of the residue showed the signals of **21b** (45%) and **16b** (20%).

1-Dimethylamino-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**19c**): To a solution of 45 mg (0.07 mmol) of **5b** in 0.5 ml of dichloromethane, 8 mg (0.07 mmol) of *N*-trimethylsilyldimethylamine was added. The ^{31}P-NMR spectrum of the orange solution shows the signals of **19c** as the main product.

1-Diethylamino-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**19d**): To a suspension of 0.82 g (1.2 mmol) of **5b** in 10 ml of dichloromethane, 0.2 g (1.5 mmol) of Me_3SiNEt_2 was added. After 1 h all volatiles were removed in vacuo. The ^{31}P-NMR spectrum of the residue showed the signals of **19d**.

1-Chloro-3-morpholino-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Chloride (**16e**) *and 1,3-Bis(morpholino)-2-triphenylphosphonio-4-triphenylphosphoranediyl)-1,3-diphosphetane Chloride* (**20e**): To a solution of 49 mg (0.07 mmol) of **5b** in 0.5 ml of dichloromethane, 7 mg (0.07 mmol) of morpholine was added. The ^{31}P-NMR spectrum of the orange solution showed the signals of **16e**. The same solution with 64 mg (0.73 mmol) of morpholine gave the signals of **20e**.

1-Morpholino-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**19e**): To a solution of 1.44 (2.11 mmol) of **5b** in dichloromethane, 0.65 g (4.20 mmol) of *N*-trimethylsilylmorpholine was added dropwise. After stirring for 18 h all volatiles were removed in vacuo and the residue was recrystallized from a 1:1 mixture of benzene and dichloromethane. – Yield 1.14 g (74%) orange crystals, m.p. 197–201°C (decomp.) – ^{1}H NMR (CH_2Cl_2/C_6D_6, 4:1): δ = 7.88 (m, 18H, *o*-, *p*-H), 7.79 (m, 12H, *m*-H), 5.33 (CH_2Cl_2), 3.23 (m, 4H, OCH_2), 2.73 (m, 4H, NCH_2). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 133.8 (m, *o*-C), 133.3 (m, *p*-C), 129.7 (m, *m*-C), 124.9 (m, *i*-C), 109.1 (m, 2,4-C), 66.9 (m, C–O), 46.9 (m, C–N), 54.1 (q, CD_2Cl_2). – $C_{42}H_{38}ClNOP_4$ (732.12): calcd. C 68.90, H 5.23, N 1.91; found C 68.12, H 5.28, N 1.87.

1-Chloro-3-benzophenonimino-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Chloride (**16f**): To a solution of 71 mg (0.10 mmol) of **5b** in 0.5 ml of dichloromethane, 40 mg (0.21 mmol) of benzophenone imine was added. Its ^{31}P-NMR spectrum showed **16f** as the main product.

1-Benzophenonimino-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**19f**): To a solution of 0.45 g (0.65 mmol) of **5b** in 6 ml of tetrahydrofuran, 0.12 g (0.65 mmol) of *N*-trimethylsilylbenzophenone imine was added dropwise. After 2 h the solution was filtered and concentrated to a third of its initial volume. Its ^{31}P-NMR spectrum showed the signals of **19f**.

1-Diethylamino-3-butyl-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane (**24**): To a suspension of 55 mg (0.1 mmol) of **19d** in 0.5 ml of tetrahydrofuran at −78°C, 48 µl (0.1 mmol) of a 1.6 M solution of *n*-BuLi in hexane was added. The ^{31}P-NMR spectrum showed **24** as the main product.

1-Diethylamino-3-methoxy-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Chloride (**25**): To a solution of 79 mg (0.1 mmol) of **19d** in 0.5 ml of dichloromethane at −78°C, 3 mg (0.1 mmol) of methanol was added. Its ^{31}P-NMR spectrum showed the signals of **19d** and **25**.

1-Diethylamino-1-selenoxo-3-chloro-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane (**26**) and *1-Diethylamino-1-selenoxo-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Tetrachloroaluminate* (**27**): To a solution of 132 mg (0.2 mmol) of **19d** in 0.5 ml of dichloromethane, 15 mg (0.2 mmol) of selenium was added. Its ^{31}P-NMR spectrum showed the signals of **26** and, after addition of 38 mg (0.3 mmol) of $AlCl_3$ those of **27**.

1-Diphenylphosphino-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**31**): To a solution of 0.40 g (0.59 mmol) of **5b** in 4 ml of dichloromethane, 0.15 g (0.59 mmol) of Ph_2PSiMe_3 was added dropwise. The ^{31}P-NMR spectrum of the orange solution showed the signals of **31**.

1-Triphenylphosphonio-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Tetrachloroaluminate (**32**): To a solution of 73 mg (0.1 mmol) of **5b** in 0.5 ml dichloromethane at −78°C, 74 mg (0.5 mmol) of $AlCl_3$ and 54 mg (0.2 mmol) of Ph_3P were added. Its ^{31}P-NMR spectrum showed **32** as the main product.

1,3-Dichloro-1-methyl-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetanium Iodide (**33a**): To a solution of 86 mg (0.13 mmol) of **5b** in 0.5 ml of dichloromethane, 18 mg 0.13 mmol) of methyl iodide was added. The ^{31}P-NMR spectrum recorded after 1 h showed the signals of **33a**.

1,3-Dichloro-1-methyl-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetanium Methylsulfate (**33b**): To a solution of 80 mg (0.12 mmol) of **5b** in 0.5 ml of dichloromethane, 7.4 mg (0.06 mmol) of Me_2SO_4 was added. Its ^{31}P-NMR spectrum showed the signals of **33b** (50%) and **6b** (50%).

1,3-Dichloro-2-methyl-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Chloride (**34a**): To a solution of 0.52 g (1.09 mmol) of **3b** in 10 ml of tetrahydrofuran, 0.40 g (1.09 mmol) of $Ph_3P{=}C(Me)SiMe_3$ in 2 ml of tetrahydrofuran was added dropwise. After stirring for 18 h the yellow precipitate formed was filtered off and recrystallized from a 1:1 mixture of tetrahydrofuran and dichloromethane. – Yield 590 mg (74%), m.p. 140°C (decomp.)

1,3-Dichloro-2-ethyl-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diphosphetane Chloride (**34b**): To a solution of 0.59 g (1.23 mmol) of **3b** in 13 ml of tetrahydrofuran, 0.46 g (1.23 mmol) of $Ph_3P{=}C(Et)SiMe_3$ in 2 ml of tetrahydrofuran was added dropwise. After stirring for 19 h the yellow precipitate formed was filtered off and recrystallized from a 1 : 1 mixture of tetrahydrofuran and dichloromethane. – Yield 746 mg (81%), m.p. 158°C (decomp.) – $C_{40}H_{35}Cl_3P_4 \cdot 0.25\ CH_2Cl_2$ (767.21): calcd. C 63.01, H 4.66; found C 62.98, H 5.07.

1,3-Dichloro-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane Irontetracarbonyl (**35a**): 0.83 g (1.21 mmol) of **5b** and 0.44 (1.21 mmol) of $Fe_2(CO)_9$ were stirred in 15 ml of tetrahydrofuran. After 17 h the solution was filtered and evaporated in vacuo. The ^{31}P-NMR spectrum of the residue showed **35a** as the main product.

1,3-Dichloro-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane Chromiumpentacarbonyl (**35b**): To a suspension of 0.56 g (0.82 mmol) of **5b** in 5 ml of tetrahydrofuran, 13 ml of a 0.07 M solution of $Cr(CO)_5 \cdot THF$ in tetrahydrofuran was added. A ^{31}P-NMR spectrum of the solution, recorded after filtration, showed **35b** as the main product.

1-(Cyclopentadienyldicarbonyliron)-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**36a**): To a suspension of 0.59 g (0.86 mmol) of **5b** in 10 ml of tetrahydrofuran at 0°C, 10 ml of a 0.086 M solution of $Na/KFe(CO)_2Cp$ in tetrahydrofuran was added dropwise. The solution turned dark red and a precipitate formed. After stirring for 1 h at 0°C the reaction mixture was warmed to room temperature and the precipitate filtered off. Its ^{31}P-NMR spectrum showed broad signals of **36a** (80%).

1-(Cyclopentadienyltricarbonylchromium)-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium Chloride (**36b**): To a suspension of 0.35 g (0.52 mmol) of **5b** in 5 ml of tetrahydrofuran, 0.19 g (0.85 mmol) of $NaCr(CO)_3Cp$ in tetrahydrofuran was added. After stirring for 18 h the solution was reduced to half its initial volume and pentane was added. After 14 h black crystals of **36b** had separated.

Reaction of **5b** *with Methanol:* To a solution of 57 mg (0.08 mmol) of **5b** in 0.5 ml of dichloromethane at 0°C, 10 mg (0.33 mmol) of methanol was added and the $^{31}P\{^1H\}$-NMR spectrum was recorded: δ = 141.5 [s, 45%, $P(OMe)_3$], 113.4 (t), 22.0 [d, $^2J_{PP}$ = 50.8 Hz (**30**, 55%)].

Reaction of **5b** *with Phosphorus Trichloride:* To a solution of **5b** in 0.5 ml of dichloromethane (first case) or a 1 : 1 mixture of dichloromethane and benzene (other cases), PCl_3 was added. Amounts, conditions and observed results as taken from the ^{31}P-NMR spectra are given in the Table below. – ^{31}P NMR: **3b**[5]; **39** (AA'BCC', simulated by LAOCOON 5[20]), δ_A = 121.6 (1,2-P), δ_B = 82.4 (4-P), δ_C = 19.8 (PPh_3), $^1J_{AA'}$ = −260.5, $^2J_{AB}$ = 52.9, $^2J_{AC}$ = 92.4, $^3J_{AC'}$ = −7.0, $^2J_{BC}$ = 70.2 Hz; **40**[17]; **41** (Table 1).

5b (mg)	PCl_3 (mg)	molar ratio PCl_3/**5b**	temp. [°C]	time [h]	resulting molar percentage PCl_3	**3b**	**39**	**40**	**41**
130	26	1	0→25	1	23	0	17	30	30
74	15	1	50	48	15	27	6	24	28
98	10	0.5	50	1	0	0	5	44	40
90	10	0.5	50	48	4	4	8	39	36

To a solution of 76 mg (0.11 mmol) of **5b** and 21 mg (0.11 mmol) of $SnCl_2$ in 0.5 ml of dichloromethane, 15 mg (0.11 mmol) of PCl_3 was added. The ^{31}P-NMR spectrum showed mainly the signals of **42**[17] (35%) and **9b** (40%).

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