

Bis(ylide)-substituted phosphonium and phosphonium halides

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Abstract

The bis(triphenylphosphoniumylidyl)halophosphines expected from the condensation of ylidyldihalophosphines with trimethylsilyl ylides or of their addition to carbodiphosphoranes enter a spontaneous dissociation to yield bis(ylidyld)phosphonium halides. They are the first phosphonium salts which do not need anions of low basicity such as AlCl_4^- . ^{31}P NMR spectra and, in one case, a single-crystal X-ray investigation reveal an essentially planar structure of the PCPCP skeleton with *E,E*-conformation.

The bis(ylidyld)phosphonium halides are protonated at an ylidic carbon atom while at the same time the halide ion is re-associated to the central phosphorus atom. They add halogen or ortho quinones to the central phosphorus to yield the corresponding phosphonium ions. They are also oxidized by elemental sulfur or gray selenium resulting in bis(ylidyld)thio- and -seleno-phosphinyl halides. As can be shown by their solvent dependent ^{31}P NMR spectra, they dissociate in polar media to yield the first examples of chalcogenoxophosphonium halides. As revealed by another X-ray structure analysis, the conjugation in a bis(ylidyld)dihalophosphonium ion is interrupted at the central phosphorus atom.

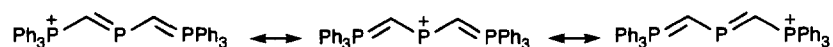
Keywords: Phosphonium halides; Phosphonium ylides; Chalcogenoxophosphonium halides; Solvent effects on ^{31}P NMR; X-ray structure investigations

1. Introduction

The first stable phosphonium ions were reported some 20 years ago [1]. Afterwards, they attracted much interest and proved to be versatile reagents [2,3]. So far, and with very few exceptions, all isolable phosphonium salts feature amino substituents and necessitate counterions of low basicity such as AlCl_4^- or CF_3SO_3^- . We now find [4] that two phosphonium ylide substituents at a halophosphine moiety can effect its spontaneous dissociation and give rise to ionic phosphonium chlorides and bromides, both in solution and in the crystalline state.



It is the first example of a non-cyclic compound for which the equilibrium lies at the side of the ionic isomer. Its stability obviously arises from the phosphonium charge being also delocalized onto the two phosphonium moieties, as shown by the resonance formulae [5]:



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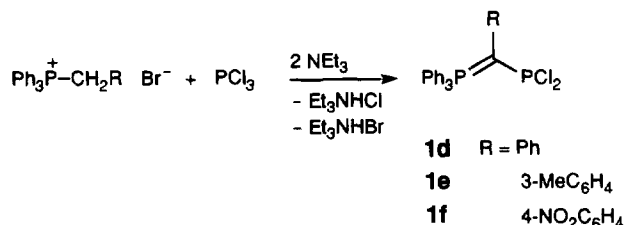
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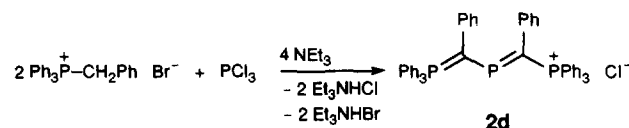
2. Results and discussion

2.1. Synthesis of bis(ylidyl)phosphenium halides

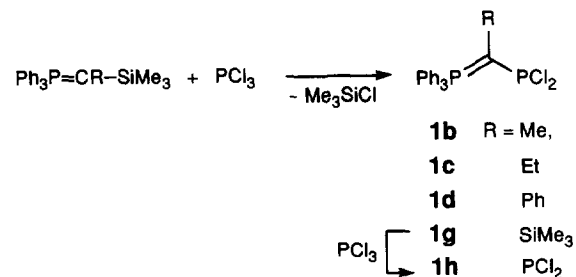
The CH_2 group of a benzyl triphenylphosphonium bromide is sufficiently acidic to react with phosphorus trichloride and triethylamine as an auxiliary base. This condensation is successfully used for the preparation of C-aryl substituted ylidyl dichlorophosphines [4,6,7] such as **1d–f**. They can be separated from the triethylammonium halides by extraction with a non-polar solvent. Ethyl and propyl triphenylphosphonium bromide do not react under the same conditions.



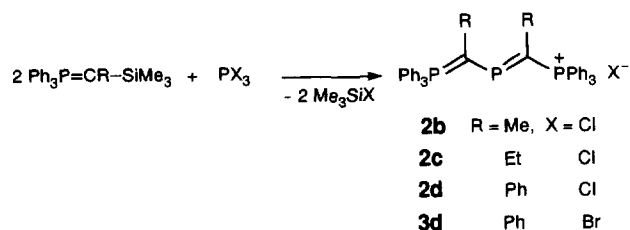
A 2:1 condensation of benzyl triphenylphosphonium bromide and phosphorus trichloride can also be achieved. As the disubstituted product **2d** proved to be ionic, however, it can no longer be separated by extraction from the triethylammonium halides. This route is therefore of no preparative use.



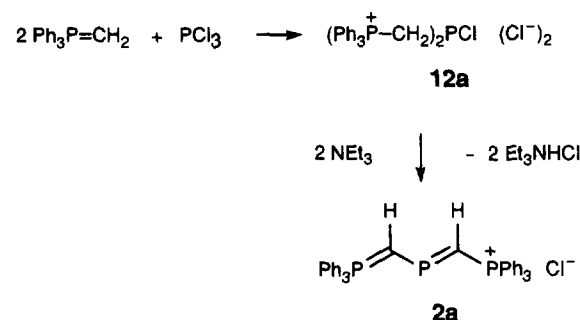
A more general route to ylidyl dichlorophosphines **1** involves the condensation of trimethylsilyl ylides $\text{Ph}_3\text{P}=\text{CR}(\text{SiMe}_3)$ with phosphorus trichloride [7]. The dichlorophosphine **1g** resulting from the bis(trimethylsilyl)ylide can react with a second mole of PCl_3 to give **1h** [8].



With a 2:1 molar ratio of trimethylsilyl ylide and phosphorus trichloride the condensation reaction yields the symmetrical bis(ylidyl)phosphenium chlorides **2** in good yields. Compound **2d** precipitates from the benzene solution in analytically pure form, and compounds **2b,c** are obtained pure by recrystallization from dichloromethane–ethyl ether mixtures. On substituting PCl_3 by PBr_3 the corresponding bromide **3d** is obtained. Proof for the ionic nature of **2d** and **3d** is provided by their identical ³¹P NMR spectra (see below).



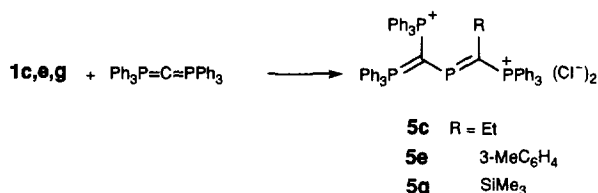
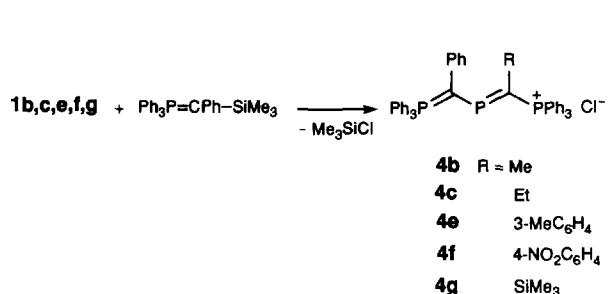
The C-unsubstituted compound **2a**, R = H cannot be prepared in this manner owing to the unspecific reaction of the respective trimethylsilylylide with PCl_3 . Its ³¹P NMR spectrum can, however, be observed when the reaction mixture obtained from methylene triphenylphosphorane and phosphorus trichloride in a 2:1 molar ratio is deprotonated by triethylamine [7].



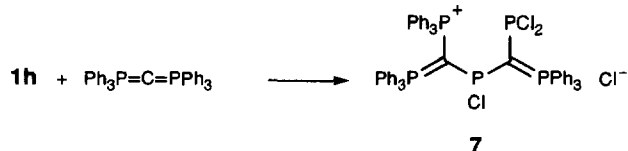
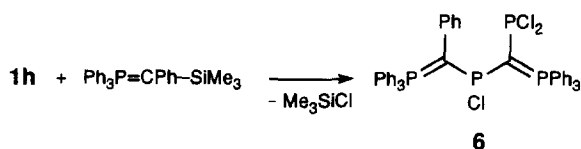
Nonsymmetrical bis(ylidyl)phosphenium chlorides **4**, **5** are obtained from ylidyl dichlorophosphines **1** and

triphenylphosphonium trimethylsilyl benzylide or hexaphenylcarbodiphosphorane.

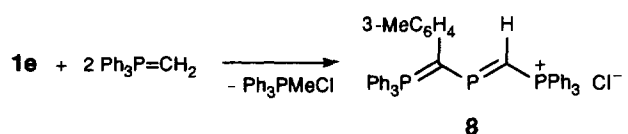
carbodiphosphorane is ionic but its cation also retains a covalent PCl bond.



In the reaction of **1f** with the benzylide a number of unidentified by-products are formed. The compound obtained from **1h** and the benzylide is not ionic but rather a covalent chlorophosphine **6**. It subsequently gets involved in an intramolecular reaction between the remaining PCl₂ group and the phenyl group to give the cation **38** (see below) [9]. Product **7** from **1h** and the



The bis(ylidyl)phosphenium chloride **8** with one ylidic carbon atom unsubstituted is obtained from **1e** and methylene triphenylphosphorane by transylidation.



The isolated bis(ylidyl)phosphenium halides **2–5** are yellow to orange crystalline solids which may be handled in air for a short period of time. The compounds

Table 1

³¹P NMR data of symmetric (**2**, **3**) and unsymmetric (**4**, **5**, **8**) bis(ylidyl)phosphenium halides Ph₃P^B=CR–P^A=CR'–P^CPh₃⁺ X[–] in CH₂Cl₂ or as solid ^a, coupling constants *J* in Hz

	R	R'	X	δ _A	δ _B	δ _C	<i>J</i> _{AB}	<i>J</i> _{AC}	<i>J</i> _{BC}
2a	H	H	Cl	326.4	23.1		109.9		
2b	Me	Me	Cl	303.5	31.9		170.9	13.2 ^a	
2b [*]				288.4	30.8	31.0	183	165	
2c	Et	Et	Cl	295.5	30.5		169.4		13.0 ^a
2d	Ph	Ph	Cl	291.0	25.4		165.3		12.1 ^a
2d [*]				286.0	18.6	19.3	177	171	
2e	3-MeC ₆ H ₄	3-MeC ₆ H ₄	Cl	292.1	25.1		166.6		
3d	Ph	Ph	Br	290.8	25.0		166.4		
8	3-MeC ₆ H ₄	H	Cl	314.1 ^b	24.4	23.7	146.5	119.0	10.7
4b	Me	Ph	Cl	298.2	31.4	25.0	172.4	165.0	12.2
4c	Et	Ph	Cl	294.8	30.8	24.7	169.4	162.9	12.2
4e	3-MeC ₆ H ₄	Ph	Cl	291.2	24.9		164.8		
4f	4-NO ₂ C ₆ H ₄	Ph	Cl	293.3	25.6	25.3	166.3	158.7	10.7
4g	SiMe ₃	Ph	Cl	314.3	23.8	24.6	118.5	144.9	10.7
5c	Et	PPh ₃ ⁺ Cl [–]	Cl	332.6	28.0	24.0	183.1	65.1	< 3
5e	3-MeC ₆ H ₄	PPh ₃ ⁺ Cl [–]	Cl	298.4	29.5	24.1	216.7	80.1	< 3
5g	SiMe ₃	PPh ₃ ⁺ Cl [–]	Cl	373.6	21.1	21.8	161.2	48.0	8.0

^a ⁴*J*_{PP} from the simulation of the ¹³C NMR spectra. ^b ²*J*_{PH} = 10.6 Hz.

are easily soluble in dichloromethane, slightly soluble in tetrahydrofuran and are insoluble in benzene or pentane.

2.2. NMR spectra of bis(ylidyl)phosphenium cations

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Table 1) of the symmetrical bis(ylidyl)phosphenium halides **2** and **3** represent AB_2 spin systems; those of the non-symmetrically substituted derivatives **4**, **8** and **5** represent ABC and ABC_2 spin systems, respectively. The chemical shifts of the phosphonio group lie in the typical range of triphenylphosphonium salts and ylides [10]. Similar to those of other phosphonium salts [2,3] or phosphaaalkenes [11], the signals of the two-coordinate phosphorus atoms are found at low field. They are independent of the counter ion X^- , which may be Cl^- , Br^- or AlCl_4^- . The latter salt was obtained by addition of aluminum trichloride to a solution of **2d** in dichloromethane.

The coupling constants $^2J_{\text{PP}}$ (J_{AB} and J_{AC}) are relatively large and indicate a synperiplanar orientation of the electron lone pair at the central phosphorus atom and the phosphonio groups, i.e. an *E,E*-geometry of the PCPCP skeleton. Where a cyclic structure (such as **42**, see below) necessitates an antiperiplanar orientation, $^2J_{\text{PP}}$ is much smaller [12].

Assuming planarity also for the molecular skeleton of the dications **5**, the two phosphonio groups of the $\text{C}(\text{PPh}_3)_2$ unit should be non-equivalent. Instead an ABC_2 spin system is observed and indicates a low rotational barrier for the central PC-bonds. The respective coupling constant $^2J_{\text{PP}}$ (J_{AC}) is about half as large as in the other cases. It represents the average of the synperiplanar and the antiperiplanar coupling, with the latter being close to zero. An analogous case was found and discussed in more detail in a previous paper [7]. The *E,E*-conformation is confirmed by the observation of a four-bond PP-coupling constant J_{BC} for all the compounds **2–4** and **8** for which the spectra could be analyzed. For 1,3-diphosphoniopropenide cations which have *E,Z*-conformation, this coupling could not be observed [13,14].

All ^{13}C NMR signals of the symmetric compounds **2b**, **c**, **d** represent the X-part of $\text{AA}'\text{BX}$ spin systems. The signals of the ylidic carbon atoms (Table 2) and also those of the *meta*-carbon atoms of the triphenylphosphonio groups were analyzed in particular to pro-

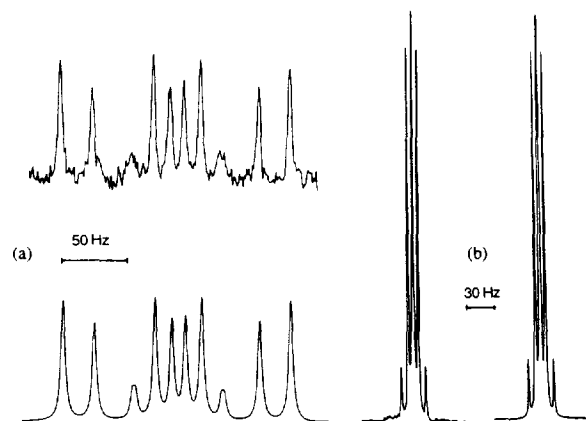


Fig. 1. ^{13}C NMR signals of **2c** in CD_2Cl_2 , $\nu_0 = 100.540$ MHz. (a) Recorded (above) and simulated (below) signal of the ylidic carbon atoms. (b) Recorded (left) and simulated (right) signal of the *meta*-carbon atoms of the *P*-phenyl rings.

vide $^4J_{\text{PP}}$ (Table 1). They were simulated by DCYMPLOT [15] (Fig. 1).

With regard to the resonance formulae of **2** the carbon atoms of their PCPCP skeleton may be compared on the one hand with those of phosphaaalkenes and on the other hand with those of triphenylphosphonium ylides. The chemical shifts of the former are found at much lower field ($\delta^{13}\text{C} = 170\text{--}210$ [11]), that of the unstabilized ylide ($\delta^{13}\text{C} = -5$ [16,17]) and also those of acylides ($\delta^{13}\text{C} = 30\text{--}60$ [16–21]) at higher field. Similar chemical shifts of the ylidic carbon atom are known in case of substitution with PS_2 or PSe_2 groups ($\delta^{13}\text{C} = 84$ and 97 respectively [22,23]). The coupling constants are found in the range known for related compounds [12–14,24–27].

2.3. Molecular structure of **2d**

Orange-red crystals of **2d** $\cdot 0.5 \text{ C}_6\text{H}_6$ were used for X-ray structure analysis. Discrete phosphonium cations and chloride anions, as disclosed for the solution from ^{31}P NMR, are also found for the crystal (Fig. 2 and Table 3). The same is true for the *E,E*-conformation of the cation. The chloride ion has no contact to the cation. The ylidic carbon atoms C1 and C2 of the cation reside each in a planar surrounding, the two planes being twisted by 17.1° against each other.

The angle at the two-coordinate phosphorus atom (C1-P2-C2) is characteristic for (acyclic) phosphonium-type compounds in contrast to the much smaller angles ($100\text{--}105^\circ$) found for 2-phosphaallylic cations [28]. Almost the same angle (114.8°) is reported for a diaminiophosphonium ion [2,3]. The angles between the phenyl rings at C1 and C2 and the phosphonium center are widened, obviously due to the steric demand of these substituents.

The central PC-bonds (P2-C1 and P2-C2) are somewhat longer than those of phosphaaalkenes ($161\text{--}171$ pm

Table 2

^{13}C NMR data of the ylidic carbon atoms of symmetric bis(ylidyl)phosphenium chlorides **2**, coupling constants J in Hz

	δ	$^1J(\text{P}^\text{V}\text{C})$	$^1J(\text{P}^\text{III}\text{C})$	$^3J(\text{P}^\text{V}\text{C})$
2b	85.9	87.2	67.3	28.5
2c	94.4	82.5	72.0	27.4
2d	97.1	86.6	72.5	23.7

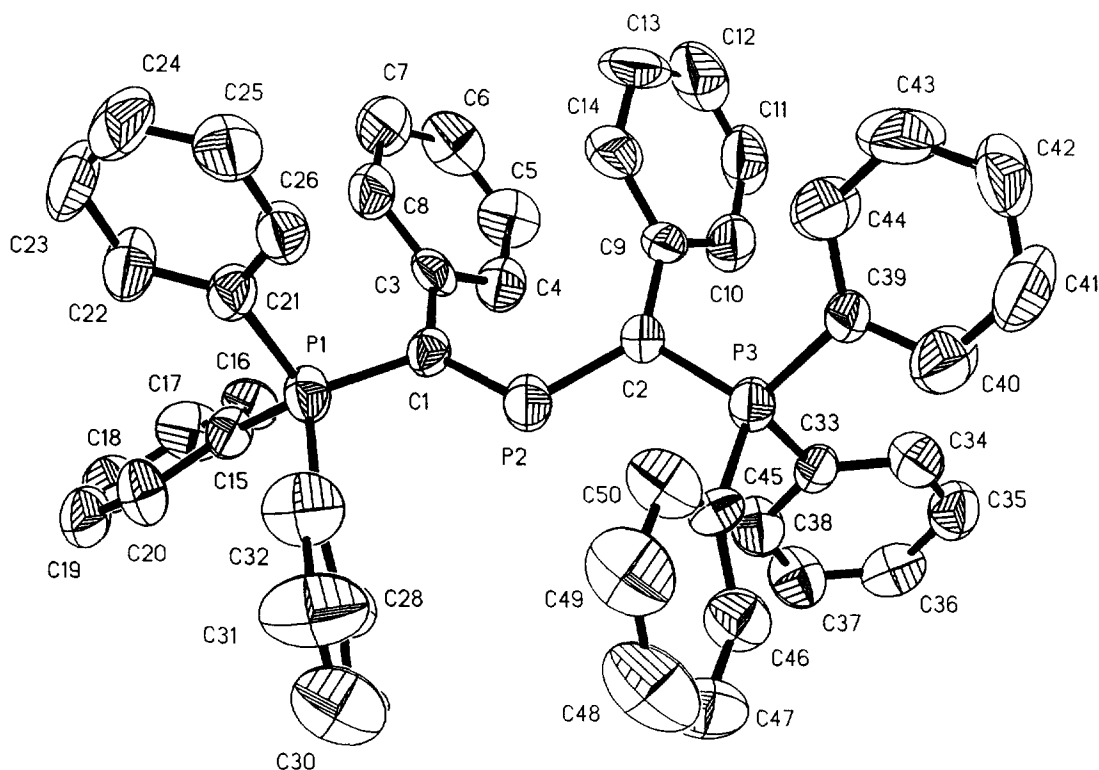


Fig. 2. Molecular structure of the cation in a crystal of **2d** · 0.5C₆H₆. Thermal ellipsoids are represented at 50% probability.

[11]), the ylidic PC-bonds are as long as those of acylides (171–175 pm [29,30]).

2.4. Reactions of bis(ylidyl)phosphenium cations

Phosphenium ions are isoelectronic to carbenes, and like them they display both electrophilic and nucleophilic behavior. For the known phosphenium ions, Lewis acid properties definitely prevail [2,3] (see Section 1). In contrast, the ionic structures of **2–5** and **8** demonstrate a much lower Lewis acidity for the bis(ylidyl)phosphenium cations. Consequently, **2d** does not react with

neutral bases like triethylamine, *N*-methylimidazole or hexamethylphosphorus triamide. Anions more basic than the chloride ion add to the central phosphorus atom of **2d** to form bis(ylidyl)phosphanes [31].

Protonation of the phosphenium chlorides by HCl or HBF₄ occurs at an ylidic carbon atom and, at the same time, the chloride ion adds to the central phosphorus. Obviously the remaining ylide substituent cannot lower the phosphenium acidity sufficiently to avoid this re-association. Protonation of **2d** by HCl in the presence of aluminum trichloride leaves the central phosphorus atom in **13** two-coordinate owing to the formation of the less basic AlCl₄[−] ion.

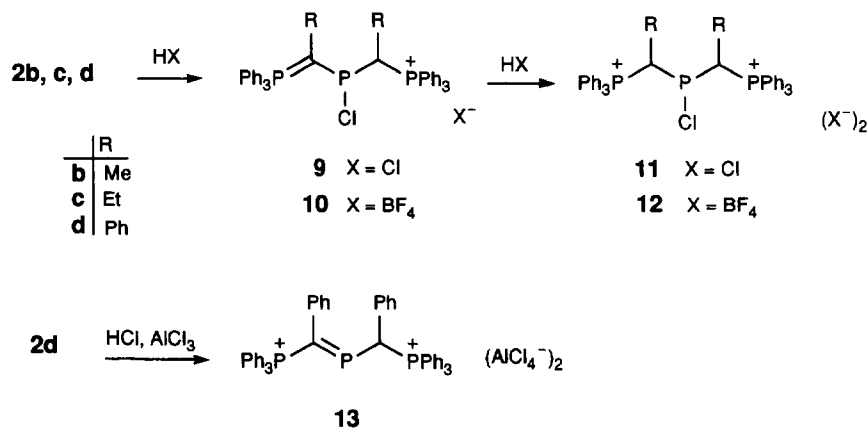


Table 3

Selected bond lengths (pm) and bond angles (deg) of the cations of compounds **2d** and **19**

	2d	19
P2–C11		205.3(4)
P2–C12		203.4(3)
P2–C1	172.4(6)	167.9(9)
P2–C2	171.4(7)	167.3(9)
P1–C1	175.3(7)	173.3(9)
P3–C2	174.6(6)	174.7(8)
P1–C15	182.3(7)	180.7(11)
P1–C21	181.7(7)	179.9(11)
P1–C27	183.7(9)	180.1(10)
P3–C33	181.6(6)	178.0(10)
P3–C39	181.4(7)	178.9(9)
P3–C45	181.3(9)	180.2(10)
C1–C3	152.9(11)	150.9(14)
C2–C9	149.0(11)	151.1(13)
C11–P2–C12		98.6(2)
C11–P2–C1		104.5(3)
C11–P2–C2		115.2(4)
C12–P2–C1		115.3(4)
C12–P2–C2		105.3(3)
C1–P2–C2	113.9(3)	117.0(5)
P1–C1–P2	112.5(4)	127.6(6)
P1–C1–C3	118.6(5)	116.6(6)
P2–C1–C3	128.4(5)	115.2(6)
P3–C2–P2	112.9(4)	127.2(6)
P3–C2–C9	115.6(5)	115.4(6)
P2–C2–C9	131.4(5)	116.2(6)

Compared with the starting compounds **2**, the ^{31}P NMR spectra (Table 4) of the monoprotonation products **9**, **10** show an ABC spin system with a decreased coupling constant $^2J_{\text{PP}}$ for the protonated ylide substituent and an increased coupling constant $^2J_{\text{PP}}$ for the remaining one.

Table 4

 ^{31}P NMR data of the protonation products

$\text{Ph}_3\text{P}^{\text{C}}=\text{CR}-\text{P}^{\text{A}}\text{Cl}-\text{CHR}-\text{P}^{\text{B}}\text{Ph}_3^+ \text{X}^-$ (**10,11**),
 $\text{Ph}_3\text{P}^{\text{C}}-\text{CHR}-\text{P}^{\text{A}}\text{Cl}-\text{CHR}-\text{P}^{\text{B}}\text{Ph}_3^{2+} (\text{X}^-)_2$ (**12,13**) and
 $\text{Ph}_3\text{P}^{\text{C}}-\text{CR}=\text{P}^{\text{A}}-\text{CHR}-\text{P}^{\text{B}}\text{Ph}_3^{2+} (\text{X}^-)_2$ (**14**) of symmetrical bis(ylidyl)phosphenium chlorides in CH_2Cl_2 , coupling constants J in Hz

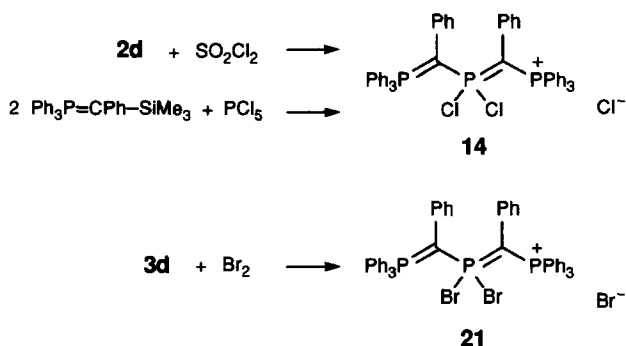
	R	X	δ_{A}	δ_{B}	δ_{C}	J_{AB}	J_{AC}	J_{BC}
9b	Me	Cl	130.1	31.0	28.5	125.2	199.9	< 3
9c	Et	Cl	129.4	30.4	27.6	148.1	225.9	< 3
10d	Ph	BF_4	110.8	28.8	24.8	39.7	201.5	6.2
11a	H	Cl	70.4	23.7		50.3		
11b	Me	Cl	92.2	30.0		93.0		
11c	Et	Cl	92.2	29.9		93.5		
12d ^a	Ph	BF_4	85.9	28.5		27.5		
			83.8	23.4		88.5		
			77.3	27.4	22.2	27.5	85.4	6.1
13d	Ph	AlCl_4	320.3	23.5	26.6	62.6	116.6	< 3

^a The ratio of the diastereomers was 10:1:1.

Protonation of the second ylidic carbon atom of **2b–d** leads to potentially diastereomeric dications. One ABC and two AB_2 spin systems are indeed observed for the RR–SS isomer and for the RrS–SrR and RsS–SsR isomers of **12d** [31] respectively. Only one isomer (A_2B spin system) is observed, however, for **11a–c**.

2.5. Bis(ylidyl)phosphenium halides

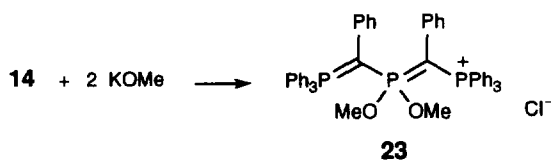
Reaction of **2d** with sulfuryl chloride yields the bis(ylidyl)dichlorophosphenium chloride **14**. Among other products, it is also formed in the reaction of the respective trimethylsilyl ylide and phosphorus pentachloride in a 2:1 molar ratio.



The bis(ylidyl)dichlorophosphenium bromide **15** and iodide **16** are formed in 50% yield when **2d** is allowed to react with Br_2 or I_2 , or in nearly quantitative yield when in addition an equimolar amount of trimethylphenylammonium chloride is present.

The bis(ylidyl)dibromophosphenium bromide **21** is formed in the reaction of **3d** with bromine at -40°C . It is unstable at room temperature. Even less stable is the bis(ylidyl)diiodophosphenium triiodide **22**. Its formation can be observed when **2d** is treated with an excess of iodine at -78°C .

The dichlorophosphenium chloride **14** is remarkably unreactive. It can be handled in moist air and does not react with methanol, water or even aqueous sodium hydroxide solution. With potassium methylate in methanol a slow reaction was observed to yield the dimethoxyphosphenium salt **23**.

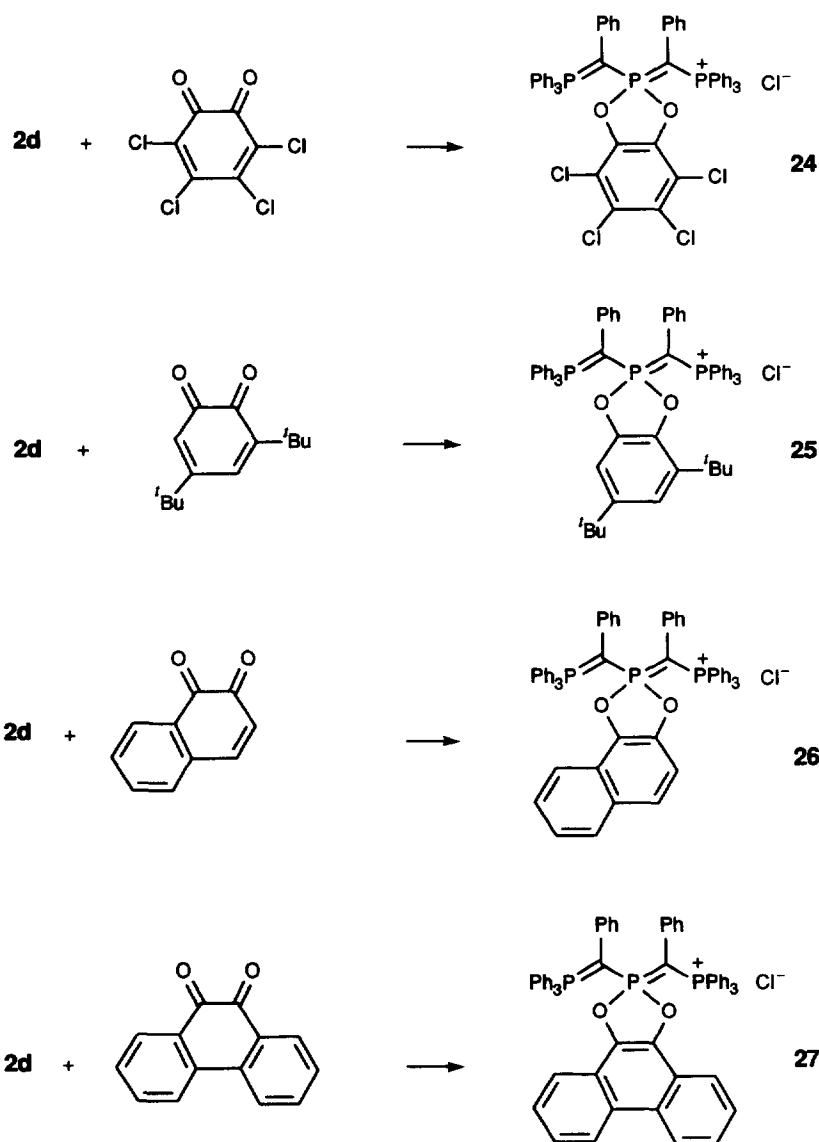


The chloride ion of compound **14** may be exchanged for BPh_4^- , BF_4^- , SbCl_6^- and TeCl_6^{2-} to yield the salts **17–20**. Most of these crystallize as thin needles, except

for the hexachloroantimonate **19** which forms crystals suitable for an X-ray structure determination (see below).

In contrast to diaminophosphenium ions [2,3], **2d**

does not react with 2,3-dimethyl butadiene. Reactions of **2d** with orthoquinones proceed exclusively by 4 + 1 cycloaddition and yield the anellated bis(ylidyl)-1,3,2-dioxaphospholenium salts **24–27**.



The ^{31}P NMR spectra of all bis(ylidyl)phosphonium ions (Table 5) represent AB_2 spin systems with the chemical shift of the central phosphorus atom in the expected range [10] and with a reduced coupling J_{AB} compared with the starting compounds **2d** [7,23,31].

2.6. Molecular structure of **19**

Fig. 3 shows the structure of the dichloro-bis(ylidyl)phosphonium cation from the X-ray structure analysis of the hexachloroantimonate **19**. The ylidic carbon atoms C1 and C2 are surrounded in a nearly planar manner (Table 3). In contrast to the almost

Table 5

^{31}P NMR data of symmetrical dihalo- and dimethoxy-bis(ylidyl)phosphonium halides and anellated bis(ylidyl)-1,3,2-dioxaphospholenium chlorides $\text{Ph}_3\text{P}^{\text{B}}=\text{CR}-\text{P}^{\text{A}}\text{Y}_2=\text{CR}-\text{P}^{\text{B}}\text{Ph}_3^+ \text{X}^-$ in CH_2Cl_2 , coupling constants J in Hz

	Y_2	X	δ_{A}	δ_{B}	J_{AB}
14 ^a	Cl_2	Cl	45.3	25.5	58.0
21	Br_2	Br	2.0	25.8	59.5
22	I_2	I_3	-23.3	26.4	61.1
23	$(\text{OMe})_2$	Cl	68.2	22.1	47.3
24	$\text{O}_2\text{C}_6\text{Cl}_4$	Cl	89.8	23.0	48.8
25	$\text{O}_2\text{C}_6\text{H}_2^t\text{Bu}_2$	Cl	84.3	23.1	50.2
26	$\text{O}_2\text{C}_{10}\text{H}_6$	Cl	86.9	22.3	48.8
27	$\text{O}_2\text{C}_{14}\text{H}_8$	Cl	88.5	23.2	48.9

^a The salts **15–20** exhibit the same ^{31}P NMR data as **14**.

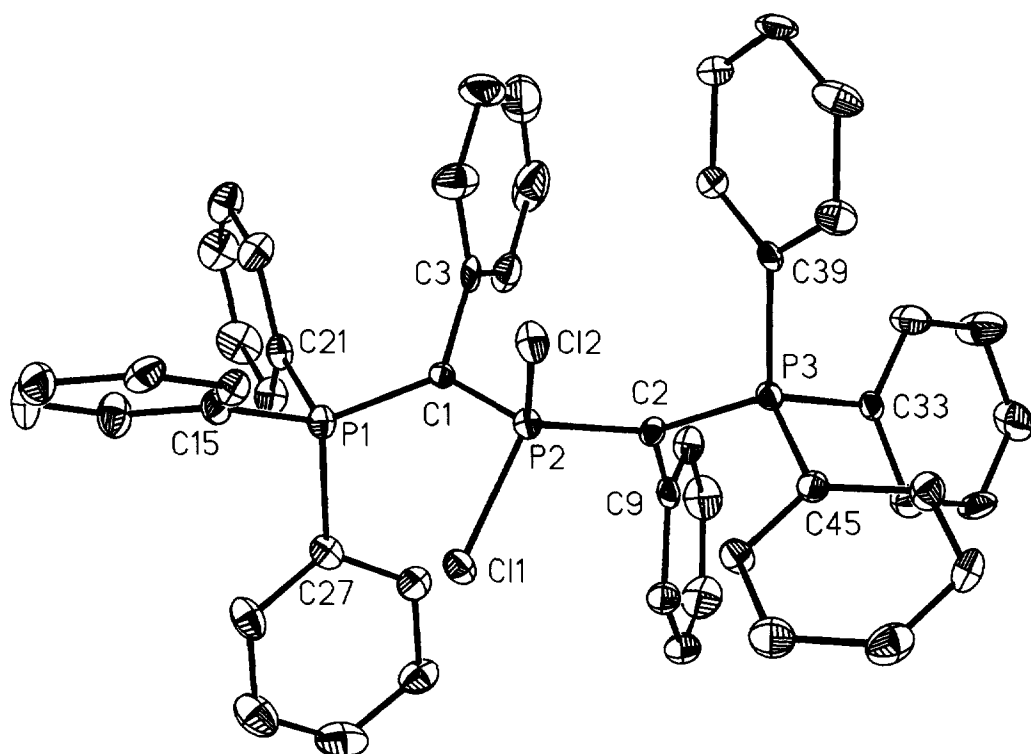


Fig. 3. Molecular structure of the cation in a crystal of **19**. Thermal ellipsoids are represented at 25% probability.

coplanar ylide moieties in **2d**, and in accord with the loss of conjugation in **19**, the two planes P1–C1–P2 and P2–C2–P3 are much more twisted against each other. The central phosphorus atom P2 has a distorted tetrahedral environment. The angle C1–P2–C2 between the two ylidic carbon atoms is much larger than the angle Cl1–P2–Cl2 between the two chlorine atoms. The ylidic bonds P1–C1 and P3–C2 in **19** have remained as long as in **2d**, whereas the bonds P2–C1 and P2–C2 (mean values) have decreased from 171.9(7) pm in **2d** on oxidation of P2 to 167.6(9) pm in **19**. Also, all bonds of P1 and P3 to the *ipso*-carbon atoms of the phenyl groups have become somewhat shorter, from 182.0(1) to 179.6(11) pm on average.

Although the sum of angles at the ylidic carbon atoms in **19** remains greater than 359°, as in **2d**, the individual angles change significantly. The PCP angles widen, while the two PCC angles at the same carbon

atom, which are quite different in **2d**, become fairly equal. As the two *C*-phenyl groups are no longer eclipsed in **19** as they are in **2d** (see discussion there), they no longer cause a distortion.

There are no significant contacts between the cation and the SbCl_6^- anion. The average SbCl bond length is 233.2(7) pm.

2.7. Bis(ylidyl)thio- and -selenophosphinyl halides / bis(ylidyl)thio- and -selenoxophosphonium halides

In a base-catalyzed reaction the phosphonium center of **2d** or **3d** can be also oxidized by elemental sulfur or selenium. The products **26–30** form yellow crystals. Depending on whether the dissociation persists or not, they must be regarded as ionic bis(ylidyl)chalcogenoxophosphonium halides or as covalent bis(ylidyl)phosphinyl halides.

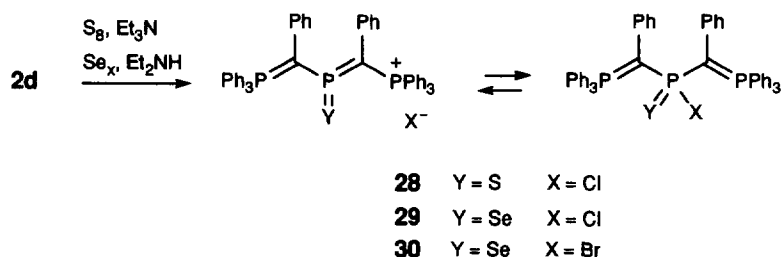


Table 6

^{31}P NMR data of compounds **28** and **29** (AB_2 spin systems) in different mixtures of dichloromethane and benzene- d_6 , and of **28** at different temperatures T , coupling constants J in Hz

T (°C)	CH_2Cl_2 (vol.%)	28			29			
		δ_{A}	δ_{B}	J_{AB}	δ_{A}	δ_{B}	J_{AB}	$^{\dagger}J_{\text{SeP}}$
+25	100.0	202.0	24.0	62.6	196.6	24.1	68.7	847.2
+25	83.3	196.2	23.6	61.1	193.2	24.0	67.1	850.0
+25	66.7	176.0	23.0	62.5	179.5	23.7	67.2	^a
+25	50.0	143.5	22.0	61.0	173.0	23.4	67.1	^a
+25	33.3	106.8	20.8	58.0	118.7	21.9	64.1	^a
+25	16.7	90.8	20.4	56.5	73.4	20.6	61.0	717.2
+50	50.0	131.5	21.6	59.5				
+25	50.0	145.4	22.0	60.2				
0	50.0	162.5	22.6	61.0				
–20	50.0	177.0	23.0	61.0				
–40	50.0	189.0	23.3	61.1				

^a Broad signals, ^{77}Se satellites are not observed.

The ^{31}P NMR spectra of **28** and **29** turn out to be strongly dependent on the solvent polarity. In dichloromethane solution an AB_2 spin system is shown with a chemical shift δ_{A} around 200 (Table 6), indicating the ionic form with a three-coordinate phosphonium center. The ionic nature is confirmed by the fact that aluminum trichloride added to the solution does not alter the spectrum, and also by the fact that the bromide **30** gives a spectrum identical to that of the chloride **29**.

While **28** and **29** are insoluble in non-polar solvents like benzene, they readily dissolve in mixtures of benzene and dichloromethane up to a volume ratio of about 5 : 1. The signal of their central phosphorus atom, which appears as a well-resolved triplet in dichloromethane, broadens and loses its fine structure with the addition of benzene, and, at the same time, moves to higher field. These findings are in accord with a mobile equilibrium between the ionic and the covalent forms which shifts to the side of the latter with decreasing polarity of the solvent. In the mixture with highest benzene content the signal is a sharp triplet again, and its chemical shift reaches $\delta_{\text{A}} = 91$ (**28**) and 73 (**29**). The slopes in Fig. 4 suggest that these shifts are already close to those of the covalent form. The same conclusion is to be drawn from the exchange broadening of the signal. This reaches its maximum for intermediate solvent mixtures when about equal amounts of the ionic and the covalent forms participate in the exchange equilibrium. The sharp signals in solvents of low and high dichloromethane content, however, indicate the exchange equilibrium mixture to contain just a small percentage of the ionic or of the covalent form respectively.

The chemical shifts and the line widths also depend on the temperature. The signal of the central phosphorus atom of **28**, dissolved in a 1 : 1 mixture of benzene and

dichloromethane, moves to higher field on warming to 50°C and to lower field on cooling to –40°C (Table 6), indicating an increased dissociation at lower temperatures. This may be rationalized by a negative entropy of dissociation due to an increased order of the solvent molecules [32]. At lower temperatures the signal becomes broader due to the decreasing exchange rate.

The signals of the triphenylphosphonio groups are less affected by the change of solvent polarity and temperature (Table 6).

The ionic forms of **33–35** are the first examples of chalcogenoxophosphonium halides. Moreover, they represent the only three-coordinate phosphonium ions known as halides. Diaminothioxophosphonium salts with PF_6^- [33] and AlCl_4^- [34–36] as counter ions have been observed, or at least been suggested, to be present in solution. Earlier, chalcogenoxophosphonium cations were postulated to occur as intermediates in the arylation of POCl_3 and PSCl_3 under Friedel–Crafts conditions and were sought by ^{31}P NMR and IR spectroscopy [37–39].

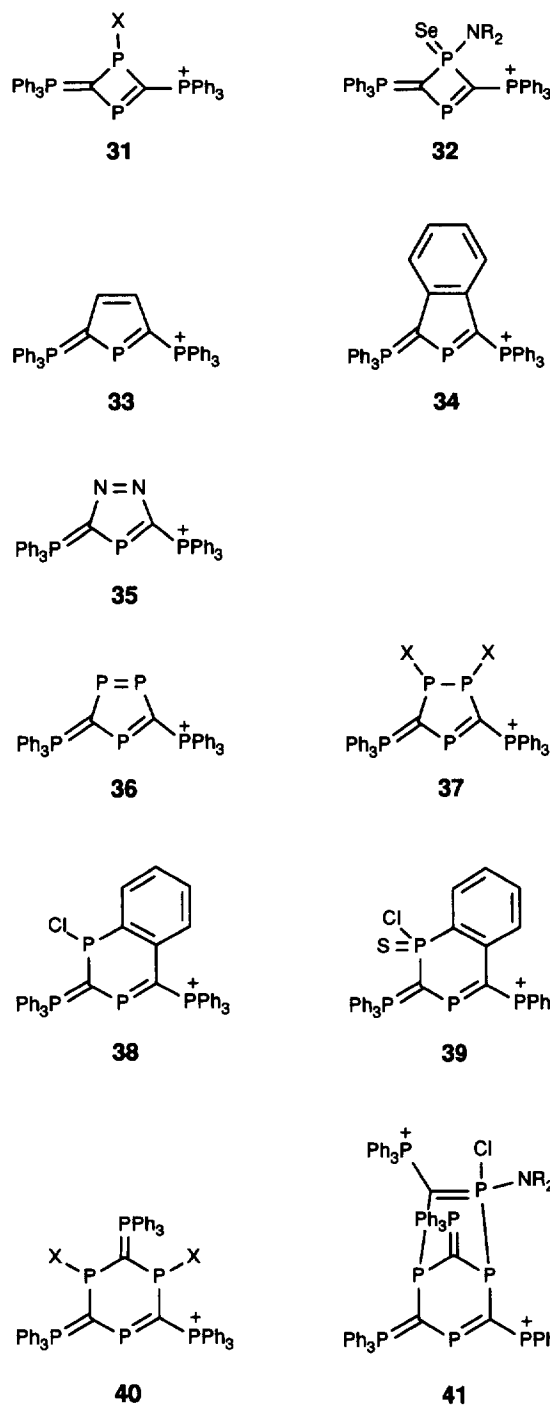
Other examples of three-coordinate phosphonium cations are provided by iminophosphonium and methylene phosphonium salts. Again, they are only known with AlCl_4^- [34,40–44] as the counter ion in the first case and with AlCl_4^- [45–47], SnCl_3^- [45] and CF_3SO_3^- [48] in the latter.

3. Conclusion and comparison with cyclic systems containing the bis(ylidyl)phosphenium moiety

Triphenylphosphonium ylide substituents exert a stronger stabilizing effect on a phosphenium center than amino substituents. Bis(ylidyl)halophosphines consequently dissociate spontaneously, and the resulting bis(ylidyl)phosphenium ions are in general only moderate Lewis acids. Even after oxidation to bis(ylidyl)-chalcogenoxophosphonium ions, the halide ion is reassociated only in part and the dissociation equilibrium can readily be shifted towards the ionic form.

The open chain bis(ylidyl)phosphenium ions discussed here may be compared with cyclic compounds in which the central CPC moiety has become part of a ring, and perhaps also part of a cyclic π -system. One of them, the 1,3-diphosphonio isophosphindolide cation **34** was in fact the first example of a bis(ylidyl)phosphenium ion [4b,49] and has been investigated since then, especially with regard to its ability to form complexes [50–52]. The cations **2** and **34** resemble each other in their low Lewis acidity, but they seem to be different in their nucleophilic behavior. While **2** is protonated at the ylidic carbon atoms, **34** is protonated at the central phosphorus atom [4b,49] and, in contrast

to **2** no oxidation of **34** has so far been achieved with sulfur or selenium.



Diphosphonio phospholide **33** [4b,53], diazaphospholide **35** [54] and triphospholide **36** [54,55] cations are all stable as simple halides and do not form covalent associates with their counter ions. This is the case, however, if halogen is added to the diphosphene unit in **36** to give **37** [54–56].

The molecular structures determined for most of the five-membered cations by X-ray analysis [51,55,57]

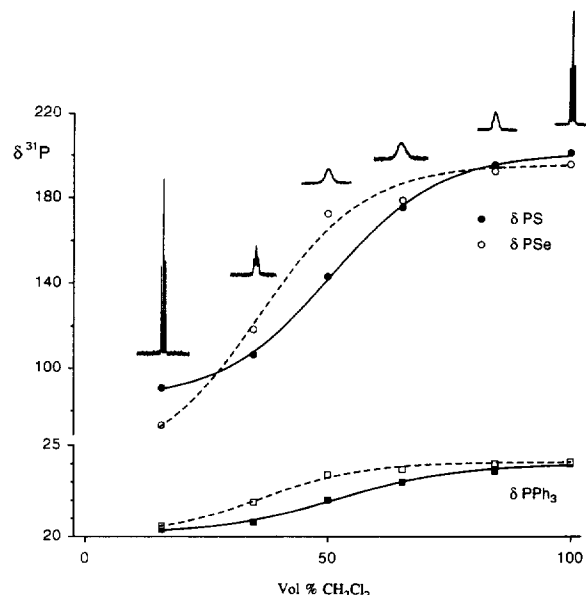


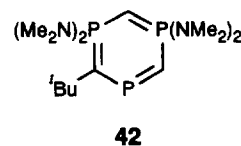
Fig. 4. Chemical ³¹P-shifts of the central phosphorus atom (above) and of the phosphonio groups (below) of **28** (filled circles and squares, solid lines) and of **29** (open circles and squares, dashed lines) in different mixtures of C₆H₆ and CH₂Cl₂. The curves result from a non-linear regression. The signals shown are those of the central phosphorus atom of **28** in the respective solvent mixture. They represent the A-part of an AB₂ spin system. The frequency scale is kept the same for all of them.

show no significant differences compared with the acyclic cation **2d**, except of course for the smaller angle at the central phosphorus atom.

In the case of the cations **31** based on a 1,3-diphosphetane ring, the phosphonium acidity depends on the nature of the substituent X at the second phosphorus ring member: with X = NR₂, PR₂, CRPPh₃ their chlorides are ionic, with X = Cl, Br, however, they form covalent halides and become ionic only with counter ions such as AlCl₄[−]. The same holds for the oxidized cation **32** [4b,54,58].

The 1,3-diphosphanaphthalene system of **38** has been mentioned in Section 2.1 to result from an intramolecular condensation of the acyclic intermediate **6**. The cation **38** forms in a spontaneous dissociation of the respective covalent chloride in a polar solvent. The dication with a π¹⁰ delocalization can be achieved with GaCl₄[−] as the counter ion [9].

The 1,3,5-triphosphinine-derived cations **40** [54,58] and **41** [54] also form in a spontaneous dissociation from their chlorides or bromides.



Finally, the neutral $1,3\lambda^5,5\lambda^5$ -triphosphinine **42** [12,59] should be mentioned. It can be compared with the bis(ylidyl)phosphenium cations as its ring also contains a sequence of two terminal four-coordinate and a central two-coordinate phosphorus atoms joined to each other by three-coordinate carbon atoms. In contrast, the chain in **42** has a *Z,Z*-structure, and this is reflected by the coupling constant $^2J_{PP}$ as discussed in Section 2.2.

4. Experimental

4.1. General

All manipulations were carried out in flame-dried glassware under dry argon using Schlenk techniques. Dry dichloromethane and benzene were used as obtained (Fluka). Pentane and diethyl ether were dried over molecular sieve (4 Å). Melting points were measured in sealed capillaries.

NMR: Jeol GSX 270 (^{31}P , ^{77}Se), Jeol EX 400 (^1H , ^{13}C) with Me_4Si (int.), 85% H_3PO_4 (ext.) and Me_2Se (ext.) as standards. NMR data are given in Tables 1, 2, 4, 5 and 6. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra m^* means X-part of AA'BX spin systems. The atoms of Ph_3P groups are identified as *o,m,p*-H and *i,o,m,p*-C, the atoms of C-phenyl groups as 2,3,4-H and C-1,2,3,4.

PCl_3 and SO_2Cl_2 were distilled prior to use. Triphenylmethylene phosphorane [60] was prepared from methyltriphenylphosphonium bromide (Merck) and sodium bis(trimethylsilyl)amide [61] in benzene. The silylated ylides $\text{Ph}_3\text{P}=\text{CRSiMe}_3$, $\text{R} = \text{Me, Et, Ph, SiMe}_3$ [7,62,63,65,66a] and hexaphenylcarbodiphosphorane [64,66b] were prepared as described in the literature.

4.2. Preparation of bis(ylidyl)phosphenium halides and bis(ylidyl)halophosphines

2b. A solution of 3.84 g (10.6 mmol) of 1-trimethylsilyl ethylene triphenylphosphorane and 0.72 g (5.3 mmol) of phosphorus trichloride in 40 ml of benzene was refluxed for 15 h. The pale yellow solution was decanted from the brown oil, which was washed three times with 50 ml portions of benzene. The oil was dissolved in 5 ml each of dichloromethane and benzene. From this solution dark yellow crystals of **2b** · CH_2Cl_2 precipitated at -30°C . Yield 2.71 g (70 %), m.p. $195\text{--}198^\circ\text{C}$ (decomp.)

Analysis calcd. for $\text{C}_{41}\text{H}_{38}\text{Cl}_3\text{P}_3$ (730.03): C, 67.46; H, 5.25; found: C, 66.89; H 5.38. ^1H NMR (CD_2Cl_2): $\delta = 2.42$ (dd, $^3J_{\text{PH}} = 4.6$ Hz, 6H, CH_3), 5.33 (s, 2H, CH_2Cl_2), 7.46–7.53 (m, 24H, *o,m*-H), 7.62 (m, 6H, *p*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 18.8$ (m^* , CH_3), 54.0 (s, CH_2Cl_2), 85.9 (m^* , CPh_3), 123.4 (m^* , *i*-C), 129.1 (m^* , *m*-C), 133.1 (s, *p*-C), 133.9 (m^* , *o*-C).

2c. A solution of 3.50 g (9.3 mmol) of 1-trimethylsilyl propylidene triphenylphosphorane and 0.64 g (4.6 mmol) of phosphorus trichloride in 20 ml of benzene was refluxed for 15 h. The pale yellow solution was decanted from the red oil, which was washed three times with 50 ml portions of benzene. The oil was dissolved in 5 ml of dichloromethane and 3 ml of diethyl-ether. From this solution, yellow crystals of **2c** · 2 CH_2Cl_2 precipitated at -30°C . Yield 2.53 g (65%), m.p. $194\text{--}197^\circ\text{C}$.

Analysis calcd. for $\text{C}_{44}\text{H}_{44}\text{Cl}_5\text{P}_3$ (843.03): C, 62.69; H, 5.26; found: C, 61.80; H 5.33. ^1H NMR (CD_2Cl_2): $\delta = 0.93$ (t, 7.3 Hz, 6H, CH_3), 2.60 (m, 4H, CH_2), 5.33 (s, 4H, CH_2Cl_2), 7.47–7.56 (m, 24H, *o,m*-H), 7.63 (m, 6H, *p*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 17.6$ (s, CH_3), 24.9 (m^* , CH_2), 54.0 (s, CH_2Cl_2), 94.4 (m^* , CPh_3), 123.7 (m^* , *i*-C), 128.9 (m^* , *m*-C), 133.1 (m^* , *p*-C), 134.0 (m^* , *o*-C).

2d. A solution of 22.70 g (45.2 mmol) of 1-trimethylsilyl benzylidene triphenylphosphorane and 3.10 g (22.6 mmol) of phosphorus trichloride in 150 ml of benzene was stirred at room temperature for 3 days. The yellow precipitate was filtered off, washed three times with 50 ml portions of benzene and dried in vacuo. Yield 16.5 g (95%), m.p. $201\text{--}203^\circ\text{C}$.

Analysis calcd. for $\text{C}_{50}\text{H}_{40}\text{ClP}_3$ (769.25): C, 78.07; H, 5.24; found: C, 78.41; H 5.49. ^1H NMR (CD_2Cl_2): $\delta = 6.47$ (m, 4H, 2-H), 6.60 (m, 4H, 3-H), 6.72 (m, 2H, 4-H), 7.36–7.42 (m, 12H, *o*-H), 7.42–7.48 (m, 12H, *m*-H), 7.63 (m^* , 6H, *p*-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 97.1$ (m, CPh_3), 123.6 (m^* , *i*-C), 125.8 (s, C-4), 127.8 (s, C-3), 128.9 (m^* , *m*-C), 133.3 (s, *p*-C), 134.4 (m^* , *o*-C), 135.7 (m^* , C-1).

3d. A solution of 6.81 g (148 mmol) of 1-trimethylsilylbenzylidene triphenylphosphorane and 2.00 g (7.4 mmol) of phosphorus tribromide in 50 ml of benzene was stirred at room temperature for 1 day. The pale yellow solution was decanted from the yellow oil, which was washed three times with 50 ml portions of benzene. The oil crystallized on stirring after addition of pentane. The yellow precipitate was filtered off and dried in vacuo. Yield 5.10 g (85%), purity approximately 97%.

5c. A solution of 3.66 g (6.8 mmol) of hexaphenylcarbodiphosphorane in 20 ml of dichloromethane was added dropwise to a solution of 2.76 g (6.8 mmol) of **1c** in 15 ml of dichloromethane at 0°C . After stirring the orange solution for 1 h at room temperature, all volatiles were removed in vacuo. The oily residue was washed three times with 50 ml portions of benzene. It crystallized slowly on drying in vacuo. Yield 6.29 g (97%), yellow, microcrystalline powder.

7. A solution of 4.30 g (8.0 mmol) of hexaphenylcarbodiphosphorane in 25 ml of dichloromethane was added dropwise at -78°C to a solution of 3.30 g (6.9 mmol) of **1h** in 20 ml of dichloromethane. After stirring the resulting yellow solution for 36 h at room tempera-

ture, all volatiles were removed in vacuo. The yellow residue was dissolved in 15 ml of dichloromethane and 35 ml of benzene. From this solution, pale yellow crystals of **7** · CH₂Cl₂ precipitated. Yield 4.29 g (57%), decomposes above 170°C.

Analysis calcd. for C₅₇H₄₇Cl₆P₅ (1099.59): C, 62.26; H, 4.31; found: C, 61.36; H, 4.93. ¹H NMR (CDCl₃): δ = 5.33 (s, 2H, CH₂Cl₂), 7.24–7.68 (m, 45 H, arom. H). ³¹P{¹H} NMR: (CD₂Cl₂, –30°C) ABCDE, δ_A = 139.9, δ_B = 180.6, δ_C = 18.6, δ_D = 29.3, δ_E = 22.0, J_{AB} = 5.0, J_{AC} = 132.0, J_{AD} = 216.7, J_{AE} = 39.7, J_{BC} = 7.6, J_{BD} = 3.8, J_{BE} = 48.8 Hz; (CDCl₃–C₂H₂Cl₄, +100°C) ABCD₂, δ_A = 138.3, δ_B = 179.4, δ_C = 20.4, δ_D = 25.8, J_{AB} = 4.6, J_{AC} = 147.3, J_{AD} = 130.3, J_{BC} = 6.9, J_{BD} < 5 Hz.

The ³¹P{¹H} NMR spectrum of **7** is temperature dependent; the signals of the two phosphonio groups of the C(PPh₃)₂ unit (δ_D and δ_E) undergo a coalescence above room temperature and become identical at higher temperatures. At +100°C the spectrum represents an ABCD₂ spin system.

Further representatives were characterized by ³¹P NMR spectroscopy:

4b–g. In an NMR tube, equimolar amounts (approximately 0.2 mmol each) of 1-trimethylsilylbenzylidene triphenylphosphorane and the appropriate ylidyl dichlorophosphine **1** were dissolved in 0.5 ml of dichloromethane. The NMR spectra of the resulting orange solutions were recorded after approximately 5 h.

5e, 5g. Formed as described for **4b** from equimolar amounts (approximately 0.1 mmol) of hexaphenyl carbodiphosphorane and the appropriate ylidyl dichlorophosphine **1**.

8. In an NMR tube, 49 mg (0.2 mmol) of methylene triphenylphosphorane were added to a solution of 42 mg (0.1 mmol) of **1c** in 0.5 ml of benzene. To the resulting yellow suspension, dichloromethane was added until a clear solution was obtained.

4.3. Preparation of bis(ylidyl)phosphonium halides

14. A solution of 0.36 g (2.7 mmol) of sulfuryl chloride in 2 ml of dichloromethane was added dropwise within 10 min at 0°C to a solution of 2.05 g (2.7 mmol) of **2d** in 10 ml of dichloromethane. After stirring the resulting pink-colored solution for 1 h, all volatiles were removed in vacuo. The oily residue slowly crystallized. Yield 2.25 g (100%), decomposes above 130°C.

Analysis calcd. for C₅₀H₄₀Cl₃P₃ (840.15): C, 71.48; H, 4.80; Cl, 12.65; found: C, 71.15; H, 4.05; Cl, 12.21. ¹H NMR (CD₂Cl₂): δ = 7.16 (m, 4H, 3-H), 7.27 (m, 2H, 4-H), 7.34–7.41 (m, 24H, *o,m*-H), 7.56 (m, 6H, *p*-H), 7.63 (m, 4H, 2-H). ¹³C{¹H} NMR (CD₂Cl₂): δ = 42.5 (m*, ¹J_{PC} = 110.0, 153.9, ³J_{PC} = 9.6 Hz, CPh₃), 124.8 (m*, *i*-C), 128.1 (m*, C-4), 128.3 (m*, C-3), 129.0 (m*, *m*-C), 133.0 (m*, *p*-C), 133.6 (m*, C-1), 134.1 (m*, *o*-C), 137.1 (m*, C-2).

17. A solution of NaBPh₄ in methanol was added dropwise to a solution of 0.79 g (1.0 mmol) of **14** in 5 ml of methanol, until no further precipitation was observed. The colorless precipitate was filtered off, washed with methanol and dried in vacuo. The crude product was dissolved in dichloromethane and the solution filtered. After concentrating and addition of diethyl ether, colorless needles precipitated. Yield 0.56 g (48%) m.p. 223–226°C.

Analysis calcd. for C₇₄H₆₀BCl₂P₃ (1123.9): C, 79.08; H, 5.38; Cl, 6.31; found: C, 78.53; H, 5.08; Cl, 6.16.

19. Prepared as described for **17** from 0.28 g (0.3 mmol) of **14** in 2 ml of methanol and a solution of (Me₃NH₃)SbCl₆ in methanol. Yield 0.20 g (53%), pale yellow crystals, m.p. 210–212°C.

Analysis calcd. for C₅₀H₄₀Cl₈P₃Sb (1139.2): C, 52.72; H, 3.54; found: C, 51.87; H, 3.68.

20. Prepared as described for **17** from 0.32 g (0.4 mmol) of **14** in 2 ml of methanol and a methanol solution of (NH₄)₂TeCl₆. Yield 0.33 g (45%) of [(Ph₃PCPh)₂PCl₂]₂TeCl₆ · 3CH₂Cl₂, colorless needles, m.p. 182–185°C.

Analysis calcd. for C₁₀₃H₈₆Cl₁₆P₆Te (2204.5): C, 56.12; H, 3.93; found: C, 55.01; H, 3.88.

21. A solution of 33 mg (0.2 mmol) of bromine in 3 ml of dichloromethane was added dropwise to a solution of 0.17 g (0.2 mmol) of **3d** in 2 ml of dichloromethane at –40°C. The ³¹P NMR spectrum of the solution recorded after 20 min at –40°C shows predominantly the signals of **21**, which, however, after 3 h at room temperature are no longer detected.

16. (a) In an NMR tube, a solution of 53 mg (0.07 mmol) of **2d** in 0.4 ml of dichloromethane was treated with 0.7 ml of a solution of iodine in dichloromethane (0.1 M, 0.07 mmol) at room temperature. The ³¹P NMR spectrum of the resulting solution shows the signals of **2d** (with Cl[–] exchanged for I[–]) and **16** in a 1:1 ratio. (b) A solution of 0.19 g (0.7 mmol) of iodine in 6 ml of dichloromethane was added dropwise to a stirred solution of 0.51 g (0.7 mmol) of **2d** and 0.11 g (0.7 mmol) of trimethylphenylammonium chloride in 10 ml of dichloromethane at 0°C. The ³¹P NMR spectrum of the resulting red solution, recorded at room temperature, shows almost exclusively the signals of **16**.

22. A solution of 0.72 g (2.9 mmol) of iodine in 20 ml of dichloromethane was added dropwise within 15 min to a stirred solution of 0.40 g (0.5 mmol) of **2d** in 4 ml of dichloromethane at –78°C. The ³¹P NMR spectrum of the resulting red solution, recorded after 30 min at this temperature, shows the signals of **16** and **22**. The latter are completely gone after 3 h at 20°C.

25. A solution of 0.42 g (1.9 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone in 2 ml of dichloromethane was added dropwise within 5 min at room temperature to a solution of 1.46 g (1.9 mmol) of **2d** in 5 ml of

dichloromethane. After stirring the yellow solution for 2 h at room temperature, all volatiles were removed in vacuo. The oily yellow residue was washed twice with benzene. On drying in vacuo it crystallized. Yield 1.88 g (100%), m.p. 136–139°C.

Analysis calcd. for $C_{64}H_{60}ClO_2P_3$ (989.56): C, 77.68; H, 6.11; found: C, 77.15; H, 6.04. 1H NMR (CD_2Cl_2): δ = 1.05 (s, 9H, $C(CH_3)_3$), 1.07 (s, 9H, $C(CH_3)_3$), 6.52 (s, 1H, arom. H), 6.62–6.65 (m, 5H, arom. H), 6.90 (m, 4H, 3-H), 6.99 (m, 2H, 4-H), 7.22–7.28 (m, 12H, *m*-H), 7.38–7.45 (m, 18H, *o*, *p*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 29.7 (s, CH_3), 31.1 (s, CH_3), 34.0 (s, CMe_3), 34.3 (s, CMe_3), 34.7 (m*, J_{PC} = 105.2, 181.0, $^3J_{PC}$ = 9.0 Hz, $CPPh_3$), 106.8 (d, J_{PC} = 9.9 Hz), 117.1 (s), 124.9 (m*, *i*-C), 126.4 (s, C-4), 127.5 (s, C-3), 128.4 (m*, *m*-C), 129.9 (d, J_{PC} = 12.6 Hz), 132.5 (m*, *p*-C), 133.6 (m*, *o*-C), 133.7 (m*, C-1), 134.4 (d, J_{PC} = 10.0 Hz), 136.5 (m*, C-2), 139.3 (s), 145.6 (d, J_{PC} = 25.6 Hz).

24, **26** and **27** were characterized by ^{31}P NMR spectroscopy. In an NMR tube, equimolar amounts (approximately 0.2 mmol) of **2d** and the appropriate 1,2-benzoquinone were dissolved in 0.5 ml of dichloromethane. The NMR spectra of these solutions were recorded after approximately 1 h. The spectroscopically estimated yield was nearly quantitative.

4.4. Reactions of bis(ylidyl)phosphenium halides with HCl and HBf_4

9, **10**. In an NMR tube, a solution of approximately 0.2 mmol of **2** in 0.5 ml of dichloromethane was treated with an equimolar amount of a solution of HCl or HBf_4 respectively, in diethyl ether at 0°C.

11b. To a stirred solution of 2.14 g (2.9 mmol) of **2b** in 20 ml of dichloromethane, 5.9 ml of a solution of hydrogen chloride in diethyl ether (1 M, 5.9 mmol) were added dropwise at 0°C within 10 min. After stirring the pale yellow solution 1 h at room temperature, all volatiles were removed in vacuo and the residue was recrystallized from dichloromethane–diethyl ether. Yield 1.81 g (82%) of **11b** · 0.5 CH_2Cl_2 , colorless crystals, m.p. 233–236°C.

Analysis calcd. for $C_{40.5}H_{39}Cl_4P_3$ (760.49): C, 63.96; H, 5.17; found: C, 64.18; H, 5.32. 1H NMR ($CDCl_3$): δ = 1.60 (m, 6H, CH_3), 5.34 (s, 1H, CH_2Cl_2), 7.08 (m, 2H, PCH), 7.57 (m, 12H, *m*-H), 7.63 (m, 6H, *p*-H), 7.83 (m, 12H, *o*-H).

11c. Formed as described for **11b** from 67 mg (0.1 mmol) of **2c** in 0.4 ml of dichloromethane and 0.2 ml of the HCl solution in diethyl ether in an NMR tube.

12d. Formed as described for **11b** from 123 mg (0.2 mmol) of **2d** in 0.5 ml of dichloromethane and 25 μ l (0.2 mmol) of HBf_4 (54% in Et_2O).

13. 45 mg (0.3 mmol) of aluminum trichloride were added to a solution of 95 mg (0.1 mmol) of **2d** in 0.5 ml

of dichloromethane in an NMR tube. Then 0.1 ml dichloromethane, saturated with hydrogen chloride, were added at –78°C.

4.5. Preparation of bis(ylidyl)chalcogenoxophosphonium halides

28. 115 mg (3.1 mmol) of sulfur were added within 5 min to a solution of 2.75 g (6.6 mmol) of **2d** in 4 ml of dichloromethane and 6 ml of triethylamine at 0°C. After 15 min stirring at room temperature, all volatiles were removed in vacuo. The residue was dissolved in 5 ml of dichloromethane and 5 ml of benzene were added. Within 1 h pale yellow needles precipitated which were filtered off, washed twice with a 2:1 mixture of benzene and dichloromethane and dried in vacuo. Yield 1.70 g (59%), decomposition above 190°C.

Analysis calcd. for $C_{50}H_{40}ClP_3S$ (801.31): C, 74.95; H, 5.03; found: C, 74.82; H, 5.15. 1H NMR (CD_2Cl_2): δ = 6.40 (m, 4H, 3-H), 6.65 (m, 4H, 2-H), 6.81 (m, 2H, 4-H), 7.47–7.51 (m, 24H, *o*, *m*-H), 7.60 (m, 6H, *p*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 67.9 (m*, J_{PC} = 104.4, 101.3, $^3J_{PC}$ = 6.7 Hz, $CPPh_3$), 133.2 (m*, *i*-C), 126.7 (s, C-4), 128.6 (s, C-3), 129.1 (m*, *m*-C), 133.3 (s, *p*-C), 134.3 (m*, *o*-C), 134.8 (m*, C-2).

29. 0.50 g (6.4 mmol) of gray selenium and 0.12 g (1.6 mmol) of diethylamine were added to a solution of 2.43 g (3.2 mmol) of **2d** in 4 ml of dichloromethane. After the reaction mixture was stirred for 3 h at room temperature, the unreacted selenium was filtered off. The filtrate was concentrated to about half of its original volume in vacuo and 8 ml of benzene were added. Within 2 h, yellow needle-like crystals precipitated, which were filtered off, washed twice with benzene and dried in vacuo. Yield 1.57 g (53%) of **29** · C_6H_6 , m.p. 144–148°C (decomp.).

Analysis calcd. for $C_{56}H_{46}ClP_3Se$ (926.32): C, 72.61; H, 5.01; found: C, 72.68; H, 5.18. $^{77}Se\{^1H\}$ NMR (CD_2Cl_2): δ = 276.7 (d, J_{SeP} = 846 Hz). 1H NMR (CD_2Cl_2): δ = 6.31 (m, 4H, 3-H), 6.65 (m, 4H, 2-H), 6.80 (m, 2H, 4-H), 7.25 (s, 6H, C_6H_6), 7.48–7.50 (m, 24H, *o*, *m*-H), 7.64 (m, 6H, *p*-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 72.9 (m*, J_{PC} = 104.4, 85.0, $^3J_{PC}$ = 8.1 Hz, $CPPh_3$), 122.8 (m*, *i*-C), 126.5 (s, C-4), 128.2 (s, C_6H_6), 128.4 (s, C-3), 128.9 (m*, *m*-C), 133.2 (s, *p*-C), 134.3 (m*, C-2), 134.4 (m*, *o*-C), 134.5 (m*, C-1).

4.6. X-ray structure analyses of **2d** and **19**

The X-ray structure determinations were performed at 293 K with a Siemens R3m/V (**2d**) and at 223 K with a Siemens P 4 (**19**) four-circle diffractometer, Mo K_α -radiation and a graphite monochromator. The programs XS (Siemens), SHELXTL PLUS and SHELXL (Sheldrick, 1993) were used for structure solution and

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2d**

x	y	z	U_{eq}	
P(1)	1122(2)	5072(1)	7589(1)	47(1)
P(2)	2292(2)	6240(2)	7683(1)	51(1)
P(3)	3361(2)	7425(1)	7720(1)	44(1)
C(1)	2431(6)	5506(3)	7426(3)	41(3)
C(2)	3321(7)	6714(3)	7330(3)	42(3)
C(3)	3435(8)	5227(3)	7011(4)	45(3)
C(4)	4742(8)	5326(3)	7255(4)	54(3)
C(5)	5652(9)	5106(4)	6877(5)	69(4)
C(6)	5328(10)	4770(4)	6277(6)	78(5)
C(7)	4053(10)	4642(3)	6020(5)	74(4)
C(8)	3101(8)	4864(3)	6402(4)	58(4)
C(9)	4205(8)	6617(3)	6779(4)	44(3)
C(10)	5519(8)	6742(3)	6932(5)	63(4)
C(11)	6308(10)	6637(3)	6406(6)	87(5)
C(12)	5845(12)	6415(4)	5748(6)	100(6)
C(13)	4550(12)	6303(4)	5574(5)	92(5)
C(14)	3729(9)	6392(4)	6095(5)	65(4)
C(15)	1528(8)	4349(3)	8014(4)	46(3)
C(16)	2707(8)	4080(3)	8010(4)	57(3)
C(17)	2930(9)	3520(4)	8330(4)	76(4)
C(18)	1997(10)	3223(4)	8630(5)	73(4)
C(19)	839(10)	3489(4)	8648(5)	75(4)
C(20)	573(7)	4925(3)	6748(4)	48(3)
C(21)	32(7)	4925(3)	6748(4)	48(3)
C(22)	−439(8)	4369(3)	6552(5)	70(4)
C(23)	−1222(9)	4279(4)	5899(5)	90(5)
C(24)	−1540(8)	4759(5)	5460(5)	85(4)
C(25)	−1082(8)	5306(4)	5632(5)	69(4)
C(26)	−296(7)	5391(3)	6271(4)	57(3)
C(27)	202(8)	5464(3)	8216(4)	50(3)
C(28)	654(8)	5478(3)	8957(5)	72(4)
C(29)	−26(10)	5772(4)	9437(5)	86(5)
C(30)	−1127(10)	6062(4)	9156(6)	95(5)
C(31)	−1598(10)	6060(5)	8444(6)	104(5)
C(32)	−943(8)	5762(4)	7954(5)	79(4)
C(33)	4796(6)	7521(3)	8383(4)	40(3)
C(34)	5596(7)	7991(3)	8389(4)	55(3)
C(35)	6659(8)	8036(4)	8936(5)	65(4)
C(36)	6863(7)	7613(4)	9484(4)	62(4)
C(37)	6046(8)	7135(4)	9463(4)	64(4)
C(38)	5046(7)	7084(3)	8912(4)	58(3)
C(39)	3252(7)	8021(3)	7045(4)	42(3)
C(40)	3238(8)	8597(4)	7271(5)	77(4)
C(41)	3122(9)	9056(4)	6757(6)	93(5)
C(42)	3025(9)	8935(4)	6038(6)	81(5)
C(43)	2955(10)	8364(4)	5804(5)	109(5)
C(44)	3060(9)	7909(4)	6317(5)	93(5)
C(45)	2021(8)	7535(3)	8220(4)	48(3)
C(46)	2213(8)	7634(3)	8966(5)	64(4)
C(47)	1158(10)	7706(4)	9329(5)	83(4)
C(48)	−26(9)	7679(5)	8946(6)	102(5)
C(49)	−230(9)	7595(4)	8197(6)	92(5)
C(50)	783(8)	7523(3)	7824(5)	65(4)
C(51)	5428(10)	5427(4)	9512(5)	73(4)
C(52)	3909(8)	4659(4)	9779(6)	77(4)
C(53)	4359(10)	5087(5)	9285(4)	80(4)
Cl	297(2)	1931(1)	9091(1)	77(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 8

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **19**

x	y	z	U_{eq}	
Sb(1)	2575.2(5)	2265.6(7)	300.7(4)	52.3(3)
Cl(8)	3421(4)	1427(4)	1144(2)	158(3)
Cl(7)	1776(3)	3119(4)	−561(3)	136(2)
Cl(6)	1604(4)	1266(4)	303(3)	156(3)
Cl(5)	2225(3)	3055(3)	1205(2)	108(2)
Cl(4)	2945(2)	1440(3)	−581(2)	88.9(13)
Cl(3)	3553(2)	3288(3)	290(2)	93.1(13)
P(1)	2839.3(15)	1857(2)	6813.8(13)	28.9(6)
P(2)	2582.2(14)	1667(2)	5207.8(12)	24.8(6)
P(3)	2275.9(13)	2237(2)	3654.6(12)	24.3(6)
Cl(2)	3358.1(15)	931(2)	4851.0(12)	35.7(7)
Cl(1)	1928.1(15)	653(2)	5448.3(12)	34.1(6)
C(21)	3225(6)	2714(7)	7439(5)	33(3)
C(22)	2776(7)	3172(8)	7770(5)	43(3)
C(23)	3102(8)	3824(8)	8263(6)	60(4)
C(24)	3859(8)	4006(8)	8408(6)	56(3)
C(25)	4311(7)	3530(8)	8067(6)	52(3)
C(26)	4004(6)	2894(8)	7594(5)	44(3)
C(27)	1862(6)	1710(7)	6863(5)	32(3)
C(32)	1642(7)	1128(8)	7309(6)	47(3)
C(31)	883(8)	1077(9)	7337(7)	62(4)
C(30)	364(7)	1625(10)	6928(7)	64(4)
C(29)	564(6)	2211(9)	6479(6)	48(3)
C(28)	1312(6)	2256(8)	6438(5)	39(3)
C(15)	3367(6)	876(7)	7170(5)	35(3)
C(20)	3506(6)	705(9)	7881(5)	50(3)
C(19)	3921(7)	−33(9)	8155(6)	58(4)
C(18)	4171(7)	−615(8)	7724(6)	51(3)
C(17)	4034(6)	−451(8)	7014(6)	43(3)
C(16)	3633(5)	286(7)	6743(5)	33(3)
C(3)	3452(6)	2952(8)	5955(4)	35(3)
C(4)	3209(7)	3794(8)	5982(6)	50(3)
C(5)	3686(10)	4505(10)	5957(8)	88(5)
C(6)	4407(11)	4325(14)	5896(8)	96(7)
C(7)	4683(9)	3482(15)	5894(7)	87(6)
C(8)	4201(7)	2777(10)	5921(6)	63(4)
C(9)	1487(5)	2844(7)	4612(5)	28(2)
C(14)	807(5)	2437(8)	4601(5)	38(3)
C(13)	184(6)	2951(10)	4653(6)	51(3)
C(12)	255(7)	3817(10)	4722(6)	57(4)
C(11)	940(7)	4234(8)	4761(6)	55(3)
C(10)	1555(6)	3745(7)	4692(5)	37(3)
C(39)	3250(5)	2348(7)	3606(5)	28(2)
C(44)	3739(5)	2871(8)	4100(5)	40(3)
C(43)	4485(6)	2986(8)	4047(6)	49(3)
C(42)	4739(6)	2621(8)	3519(6)	44(3)
C(41)	4265(6)	2118(8)	3030(6)	46(3)
C(40)	3510(6)	1966(7)	3057(5)	40(3)
C(45)	1867(5)	1271(7)	3165(5)	29(2)
C(50)	1714(6)	532(7)	3502(5)	32(3)
C(49)	1388(6)	−193(8)	3125(6)	51(3)
C(48)	1214(6)	−177(9)	2400(6)	50(3)
C(47)	1349(6)	559(8)	2059(5)	42(3)
C(46)	1683(6)	1292(7)	2430(5)	38(3)
C(33)	1782(5)	3148(7)	3174(5)	26(2)
C(38)	997(6)	3147(8)	2961(5)	41(3)
C(37)	615(6)	3879(8)	2625(6)	45(3)
C(36)	1009(7)	4588(9)	2466(7)	60(4)
C(35)	1787(7)	4582(9)	2669(8)	71(4)
C(34)	2166(6)	3869(8)	3020(6)	48(3)
C(2)	2157(5)	2296(7)	4518(4)	24(2)
C(1)	2921(5)	2186(7)	5982(5)	26(2)

Table 8 (continued)

	x	y	z	U_{eq}
C	9707(16)	5788(21)	35(16)	80(9)
Cl(10)	9674(6)	5487(8)	−736(5)	113(3)
Cl(11)	10122(6)	5134(8)	678(5)	109(3)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

refinement. Non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically (riding model). Atomic coordinates and equivalent isotropic displacement parameters for **2d** and **19** are given in Tables 7 and 8 respectively.

2d. $C_{50}H_{40}P_3Cl_3 \cdot 0.5C_6H_6$; $M = 808.2$; crystal size $0.14 \times 0.24 \times 0.36$ mm³; orange pillar, monoclinic; space group $P2_1/c$; $a = 10.568(2)$ Å, $b = 22.420(6)$ Å, $c = 18.381(5)$ Å, $\beta = 98.33(2)^\circ$, $V = 4309(2)$ Å³; $Z = 4$; $d_{calc} = 1.246$ Mg m^{−3}; $\mu = 0.231$ mm^{−1}; $F(000) = 1692$. ω -scans, 2θ -range 5 – 50° in $0 \leq h \leq 12$, $0 \leq k \leq 26$, $-21 \leq l \leq 21$; scan speed 1.5 – 14.65° min^{−1}, scan range 1.1° ; absorption correction; face indexed; numerical, max./min. transmission $0.9678/0.9423$; reflections 8571 collected, 7559 independent ($R_{int} = 0.027$), 5072 observed ($F \geq 2\sigma |F|$); $w = 1/\sigma^2 |F|$, $R = 0.0425$, $R_w = 0.0786$, 523 parameters refined; largest diff. peak/hole: $0.63/-0.56$ e Å^{−3}; GOF (on $|F|$) = 2.37. Solution by direct methods and refinement on F with the program SHELXTL PLUS (Microvax II).

19. $[C_{50}H_{40}P_3Cl_3]SbCl_6 \cdot 0.5CH_2Cl_2$, $M = 1181.5$; crystal size $0.3 \times 0.27 \times 0.26$ mm³; yellow prism, monoclinic; space group $P2_1/n$; $a = 18.039(6)$ Å, $b = 15.091(5)$ Å, $c = 19.459(6)$ Å, $\beta = 103.73(2)^\circ$, $V = 5146(3)$ Å³; $Z = 4$; $d_{calc} = 1.524$ Mg m^{−3}; $\mu = 1.132$ mm^{−1}; $\leq F(000) = 2368$. ω -scans, 2θ -range 3.5 – 45° in $0 \leq h \leq 18$, $-1 \leq k \leq 16$, $-20 \leq l \leq 20$; reflections 6843 collected, 6410 independent ($R_{int} = 0.0314$), 3938 observed ($F \geq 4\sigma |F|$). Scan speed 4 – 60° min^{−1}, scan range 1° ; max./min. transmission $0.875/0.760$. Direct methods, $R_1 = 0.0705$, $wR_2 = 0.1461$, GOF (on F^2) = 1.037, largest diff. peak/hole: $1.031/-0.779$ e Å^{−3}. The Cl atoms of the $SbCl_6$ anion are disordered. Refinement with disordered positions did not improve the result of the refinement with non-split positions. In addition, the position of the dichloromethane solvent molecule did not refine well. The freely refined site occupation factor for the CH_2Cl_2 molecule was close to 0.5, and was fixed at this value in the final steps of the refinement.

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