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A new approach to the synthesis of diazomethylenephosphoranes $\left({>}\underset{|}{P}{=}C{=}N_2 \right)$

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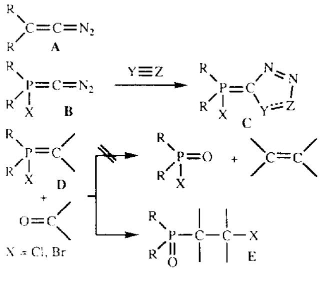
Summary – Addition of tetrachloro-*ortho*-benzoquinone to [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane **1** leads to 2-{[bis(diisopropylamino)phosphinyl]diazomethyl}-3,4,5,6-tetrachlorophenol **4** (30% yield) and the seven-membered heterocycle **5** (5% yield). Both compounds have been characterized by single crystal X-ray diffraction studies. The formation of **4** is rationalized by the transient formation of a *P*-aryloxy diazomethylenephosphorane **3**, which undergoes a Chapman-type rearrangement.

unsaturated diazo compound / diazomethylenephosphorane / Chapman rearrangement / diazophosphine / *ortho*-benzoquinone

Introduction

Unsaturated diazo derivatives **A** [1] have attracted considerable interest over the last few years mainly as potential sources of alkylidenecarbenes [2]. These compounds are highly unstable with respect to nitrogen elimination, and so far only the fluoro derivative (**A**: R = F) has been spectroscopically characterized; it appeared to be stable in a matrix below 11 K [3]. In 1987, we showed that the replacement of the carbon-carbon double bond of **A** by a phosphorus ylid functionality allowed for the isolation of pseudo-unsaturated diazo compounds **B** [4]. Since diazo derivatives [5] and Wittig reagents [6] are among the most useful synthetic building blocks, compounds **B**, which feature both of these functional groups, appeared at first glance to possess an enormous synthetic potential. Indeed, [3+2] cycloaddition reactions of the diazo moiety with a variety of dipolarophiles readily occur [7]. However, to make this synthetic route really useful, it is clear that the phosphorus part of the resulting heterocycle **C** must be easily removed, for which the Wittig reaction is certainly the best method. Unfortunately, due to the presence of the phosphorus-halogen bond, derivatives **B** and **C** do not undergo 'normal' Wittig reactions. It is indeed well known that no phosphorus-carbon bond cleavage occurs in the reaction of *P*-halogeno phosphorus ylides **D** with carbonyl groups; instead 1,3-halogen shifts are observed leading to the formation of phosphine oxides **E** [8]. So far, the only reaction known to afford diazomethylenephosphoranes is the addition of carbon tetrahalides (X = Cl, Br) to diazomethylphosphines [4,7], which is restricted to the preparation of *P*-halogenated diazomethylenephosphoranes **B** (scheme 1). Here we report our attempts to prepare halogen-free diazomethylenephosphoranes.



Scheme 1

Results and discussion

By far the simplest way to prepare a halogen-free diazomethylenephosphorane would be the direct substitution of the halogen atom of **B** by another group. However, all our attempts failed. Alternatively, Regitz *et al* [9] recently reported the synthesis of (diazoalkyl)phosphoranes **F** from [4+1]-cycloadditions of tetrahalo-*ortho*-benzoquinones to α-diazophosphines. This reaction appeared to be quite general except in the case of C-silylated diazophosphines where "the reactions were completely unselective" (scheme 2). This report prompted us to investigate in detail the reaction of

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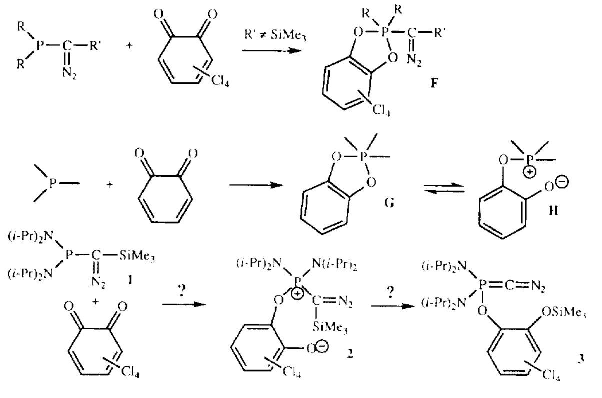
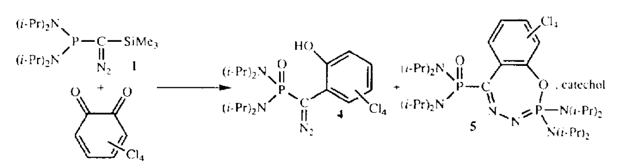
[bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane **1** [10] with tetrachloro-*ortho*-benzoquinone. Quinones are known to react with phosphines to give, depending on the phosphorus substituents, either the corresponding neutral phosphoranes **G** or alternatively the open zwitterionic compound **H** [11]. It has been shown that the presence of amino substituents at phosphorus favors the zwitterionic form **2** [11] and, because of the high affinity of silicon for oxygen, we believed that the desired diazomethylenephosphorane **3** would be obtained (scheme 2).



Scheme 2

According to ^{31}P NMR spectroscopy, a reasonably clean reaction occurred when a stoichiometric amount of tetrachloro-*ortho*-benzoquinone was added at −78°C to a THF solution of **1**. After purification by column chromatography on silica gel and recrystallization, derivatives **4** and **5** were isolated in 30 and 5% yields, respectively (scheme 3).



Scheme 3

For the major product **4**, the presence of diazo group was clearly indicated by a strong infrared absorption at 2 082 cm^{-1} and a ^{13}C NMR signal at 51.2 ppm (J_{PC} = 196.4 Hz) corresponding to a non-hydrogen-substituted diazo carbon. Moreover, the ^{31}P NMR chemical shift (+ 32.6 ppm) was in the range expected for diazomethylenephosphoranes [4, 7]. ^{1}H and ^{13}C NMR data clearly demonstrated that no trimethylsilyl group was present; it is quite understandable that the cleavage of a silicon-oxygen bond occurred during the purification by column chromatography. Since both elemental analyses and mass spectroscopic data agreed with the formulation of the phenolic derivative of **3** (a silyl group being replaced by a proton) a single crystal X-ray diffraction study was undertaken. To our surprise, this compound was not the expected diazomethylenephosphorane but the oxophosphoranyldiazo derivative **4**. The Ortep view is illustrated in figure 1 along with the atom numbering scheme, and the geometric parameters are given in table I. This structure, by itself, does not deserve much comment: the geometries of the phosphine oxide and the CN_2 part of the molecule are quite usual, and it is unsurprising that there is a hydrogen bond between the phenolic-H atom and the oxygen atom at phosphorus.

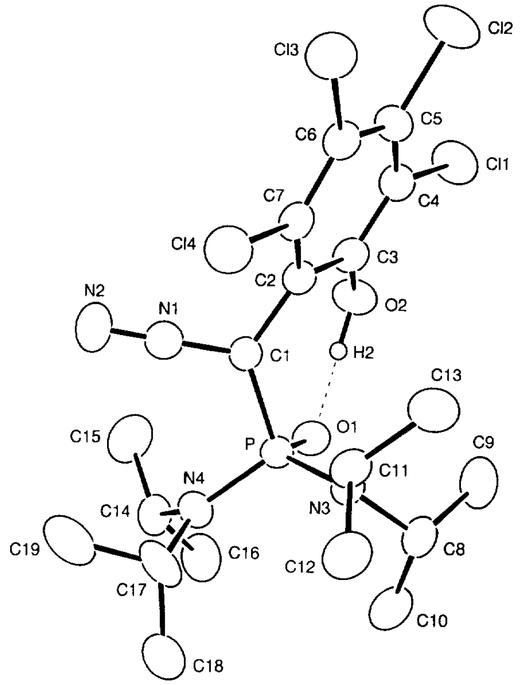


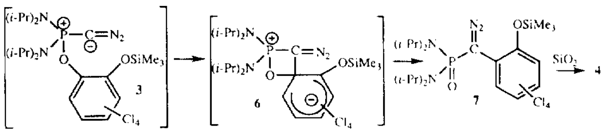
Fig 1. Ortep drawing and numbering scheme for **4**.

The presence of the aromatic ring directly bonded to the diazo carbon is rather surprising but can be rationalized as depicted in scheme 4. As expected, there is probably formation of the desired diazomethylenephosphorane **3**. In agreement with previous observations [7], which showed that the diazo carbon of diazomethylenephosphorane is strongly nucleophilic, we can imagine the attack of this negatively charged carbon on the aromatic ring (activated by the four chlorine atoms), giving intermediate **6**. After ring-opening and subsequent cleavage of the silyl group of **7** on silica gel, **4** is obtained (scheme 4). The transformation of **3** into **7** is reminiscent of the Chapman rearrangement [12] of an arylimino ester into an *N*-aryl amide, which has been proved to be intramolecular and involves a cyclic four-membered transition state [12].

The minor product **5** has two magnetically nonequivalent phosphorus atoms (δ^{31}P: 19.6 and 21.5; J_{PP} = 2.8 Hz), and no infrared absorption band characteristic of a diazo group. In the ^{13}C NMR spectrum, signals corresponding to two aromatic rings were present. Its structure was clearly established by a single crystal X-ray diffraction study, the results of which are illustrated in figure 2; the geometric parameters are given in table II.

Table I. Bond lengths (Å) and angles (deg) for compound **4**, with esds in parentheses.

P-C(1)	1.791(2)	P-N(3)	1.647(2)
P-O(1)	1.484(2)	P-N(4)	1.638(2)
C(1)-N(1)	1.319(3)	N(1)-N(2)	1.133(4)
C(1)-C(2)	1.480(3)		
C(2)-C(3)	1.412(3)	C(3)-O(2)	1.340(3)
C(3)-C(4)	1.397(3)	O(2)-H(2)	0.96(2)
C(4)-C(5)	1.382(4)	C(4)-Cl(1)	1.722(2)
C(5)-C(6)	1.389(3)	C(5)-Cl(2)	1.712(2)
C(6)-C(7)	1.385(3)	C(6)-Cl(3)	1.720(3)
C(7)-C(2)	1.396(3)	C(7)-Cl(4)	1.728(2)
N(3)-C(8)	1.498(4)	N(4)-C(14)	1.495(3)
N(3)-C(11)	1.479(3)	N(4)-C(17)	1.481(3)
C(8)-C(9)	1.519(4)	C(14)-C(15)	1.505(4)
C(8)-C(10)	1.510(4)	C(14)-C(16)	1.518(5)
C(11)-C(12)	1.528(3)	C(17)-C(18)	1.515(5)
C(11)-C(13)	1.525(4)	C(17)-C(19)	1.522(5)
C(1)-P-O(1)	107.97(9)	O(1)-P-N(3)	112.0(1)
C(1)-P-N(3)	104.4(1)	O(1)-P-N(4)	110.76(9)
C(1)-P-N(4)	107.6(1)	N(3)-P-N(4)	113.70(9)
P-C(1)-N(1)	117.8(2)	C(2)-C(1)-N(1)	114.6(2)
P-C(1)-C(2)	127.2(2)	C(1)-N(1)-N(2)	178.7(3)
C(1)-C(2)-C(7)	121.3(2)	C(4)-C(5)-C(6)	119.9(2)
C(1)-C(2)-C(3)	120.6(2)	C(4)-C(5)-Cl(2)	119.9(2)
C(7)-C(2)-C(3)	118.0(2)	C(6)-C(5)-Cl(2)	120.1(2)
C(2)-C(3)-C(4)	119.0(2)	C(5)-C(6)-C(7)	118.8(2)
C(2)-C(3)-O(2)	124.0(2)	C(5)-C(6)-Cl(3)	120.2(2)
C(4)-C(3)-O(2)	116.9(2)	C(7)-C(6)-Cl(3)	120.9(2)
C(3)-C(4)-C(5)	121.5(2)	C(6)-C(7)-C(2)	122.5(2)
C(3)-C(4)-Cl(1)	118.1(2)	C(6)-C(7)-Cl(4)	117.9(2)
C(5)-C(4)-Cl(1)	120.3(2)	C(2)- C(7)-Cl(4)	119.6(2)
C(3)-O(2)-H(2)	116(1)		
P-N(3)-C(8)	119.9(2)	P-N(4)-C(14)	121.6(2)
P-N(3)-C(11)	123.6(2)	P-N(4)-C(17)	122.4(2)
C(8)-N(3)-C(11)	116.4(2)	C(14)-N(4)-C(17)	115.9(2)
N(3)-C(8)-C(9)	112.7(2)	N(4)-C(14)-C(15)	113.5(2)
N(3)-C(8)-C(10)	113.3(2)	N(4)-C(14)-C(16)	112.7(3)
C(9)-C(8)-C(10)	111.7(3)	C(15)-C(14)-C(16)	111.1(3)
N(3)-C(11)-C(12)	113.3(2)	N(4)-C(17)-C(18)	112.3(3)
N(3)-C(11)-C(13)	112.1(2)	N(4)-C(17)- C(19)	113.4(3)
C(12)-C(11)-C(13)	110.1(2)	C(18)-C(17)-C(19)	109.7(3)
O(2)... O(1)	2.546(2)	H(2)... O(1)	1.58(2)
O(2)-H(2)... O(1)	174(2)		



Scheme 4

Table II. Bond lengths (Å) and angles (deg) for compound **5**, with esds in parentheses.

P(1)-O(1)	1.629(4)	P(2)-O(2)	1.495(4)
P(1)-N(1)	1.570(5)	P(2)-C(2)	1.832(4)
P(1)-N(3)	1.617(5)	P(2)-N(5)	1.648(5)
P(1)-N(4)	1.636(6)	P(2)-N(6)	1.640(5)
O(1)-C(1)	1.359(5)	N(1)-N(2)	1.354(6)
C(2)-C(3)	1.526(7)	N(2)-C(2)	1.301(7)
C(1)-C(3)	1.395(5)	C(3)-C(4)	1.395(5)
C(4)-C(5)	1.395(5)	C(4)-Cl(1)	1.699(4)
C(5)-C(6)	1.395(5)	C(5)-Cl(2)	1.712(4)
C(6)-C(7)	1.395(5)	C(6)-Cl(3)	1.724(4)
C(7)-C(1)	1.395(5)	C(7)-Cl(4)	1.710(4)
N(3)-C(8)	1.505(8)	N(5)-C(20)	1.492(6)
N(3)-C(11)	1.494(9)	N(5)-C(23)	1.506(7)
C(8)-C(9)	1.526(10)	C(20)-C(21)	1.527(11)
C(8)-C(10)	1.506(10)	C(20)-C(22)	1.520(10)
C(11)-C(12)	1.530(10)	C(23)-C(24)	1.520(10)
C(11)-C(13)	1.528(14)	C(23)-C(25)	1.519(10)
N(4)-C(14)	1.500(9)	N(6)-C(26)	1.498(8)
N(4)-C(17)	1.490(9)	N(6)-C(29)	1.494(7)
C(14)-C(15)	1.502(9)	C(26)-C(27)	1.522(9)
C(14)-C(16)	1.498(12)	C(26)-C(28)	1.530(9)
C(17)-C(18)	1.525(14)	C(29)-C(30)	1.52(1)
C(17)-C(19)	1.523(10)	C(29)-C(31)	1.507(8)
C(32)-C(33)	1.395(5)	C(32)-O(3)	1.360(4)
C(33)-C(34)	1.395(4)	C(33)-O(4)	1.352(6)
C(34)-C(35)	1.395(5)	C(34)-Cl(5)	1.694(4)
C(35)-C(36)	1.395(5)	C(35)-Cl(6)	1.724(3)
C(36)-C(37)	1.395(4)	C(36)-Cl(7)	1.719(4)
C(37)-C(32)	1.395(5)	C(37)-Cl(8)	1.702(4)
O(3)-H(3)	0.97(5)	O(4)-H(4)	0.97(2)
O(1)-P(1)-N(1)	112.0(2)	O(2)-P(2)-C(2)	109.0(2)
O(1)-P(1)-N(3)	112.6(2)	O(2)-P(2)-N(5)	114.5(2)
O(1)-P(1)-N(4)	98.4(2)	O(2)-P(2)-N(6)	107.1(2)
N(1)-P(1)-N(3)	108.1(3)	C(2)-P(2)-N(5)	107.8(2)
N(1)-P(1)-N(4)	116.4(3)	C(2)-P(2)-N(6)	110.4(2)
N(3)-P(1)-N(4)	109.2(2)	N(5)-P(2)-N(6)	107.9(2)
P(1)-O(1)-C(1)	121.3(3)	P(2)-C(2)-N(2)	107.2(4)
P(1)-N(1)-N(2)	127.4(4)	P(2)-C(2)-C(3)	122.9(3)
C(2)-N(2)-N(1)	124.8(4)	N(2)-C(2)-C(3)	129.6(4)
O(1)-C(1)-C(7)	116.6(3)	C(1)-C(3)-C(2)	119.7(4)
O(1)-C(1)-C(3)	123.2(3)	C(1)-C(3)-C(4)	120.0(3)
C(7)-C(1)-C(3)	120.0(3)	C(2)-C(3)-C(4)	119.0(3)
C(3)-C(4)-C(5)	120.0(3)	C(5)-C(6)-C(7)	120.0(3)
C(3)-C(4)-Cl(1)	121.3(3)	C(5)-C(6)-Cl(3)	119.9(3)
C(5)-C(4)-Cl(1)	117.8(3)	C(7)-C(6)-Cl(3)	120.0(3)
C(4)-C(5)-C(6)	120.0	C(6)-C(7)-C(1)	120.0(3)
C(4)-C(5)-Cl(2)	120.6(3)	C(6)-C(7)-Cl(4)	120.0(3)
C(6)-C(5)-Cl(2)	119.3(3)	C(1)-C(7)-Cl(4)	120.0(3)
P(1)-N(3)-C(8)	124.8(4)	P(2)-N(5)-C(20)	124.3(3)
P(1)-N(3)-C(11)	120.7(4)	P(2)-N(5)-C(23)	113.5(3)
C(8)N(3)-C(11)	114.5(5)	C(20)-N(5)-C(23)	121.9(4)
N(3)-C(8)-C(9)	113.5(4)	N(5)-C(20)-C(21)	114.3(5)
N(3)-C(8)-C(10)	113.3(6)	N(5)-C(20)-C(22)	113.4(6)
C(9)-C(8)-C(10)	111.8(6)	C(21)-C(20)-C(22)	111.0(5)
N(3)-C(11)-C(12)	111.8(6)	N(5)-C(23)-C(24)	112.9(5)
N(3)-C(11)-C(13)	111.3(7)	N(5)-C(23)-C(25)	113.9(5)
C(12)-C(11)-C(13)	110.3(7)	C(24)-C(23)-C(25)	112.5(6)
P(1)-N(4)-C(14)	127.8(4)	P(2)-N(6)-C(26)	121.9(4)
P(1)-N(4)-C(17)	114.5(4)	P(2)-N(6)-C(29)	122.1(4)
C(14)-N(4)-C(17)	114.6(6)	C(26)-N(6)-C(29)	114.8(5)
N(4)-C(14)-C(15)	114.5(4)	N(6)-C(26)-C(27)	113.0(5)
N(4)-C(14)-C(16)	112.0(7)	N(6)-C(26)-C(28)	111.0(4)
C(15)-C(14)-C(16)	113.1(6)	C(27)-C(26)-C(28)	111.1(6)
N(4)-C(17)-C(18)	111.9(5)	N(6)-C(29)-C(30)	113.2(5)
N(4)-C(17)-C(19)	110.7(7)	N(6)-C(29)-C(31)	112.6(6)
C(18)-C(17)-C(19)	110.8(8)	C(30)C(29)-C(31)	111.3(5)
C(37)-C(32)-O(3)	116.6(3)	C(34)-C(35)-C(36)	120.0(2)
C(33)-C(32)-O(3)	123.4(4)	C(34)-C(35)-Cl(6)	119.3(3)
C(37)-C(32)-C(33)	120.0(2)	C(36)-C(35)-Cl(6)	120.6(3)
C(32)-C(33)-O(4)	123.6(3)	C(35)-C(36)-C(37)	120.0(3)
C(34)-C(33)-0(4)	116.4(3)	C(35)-C(36)-Cl(7)	119.5(2)
C(32)-C(33)-C(34)	120.0(3)	C(37-C(36)-Cl(7)	120.4(3)
C(33)-C(34)-C(35)	120.0(3)	C(36)-C(37)-C(32)	120.0(3)
C(35)-C(34)-Cl(5)	120.8(2)	C(32)-C(37)-Cl(8)	118.9(2)
C(33)-C(34)-Cl(5)	119.1(3)	C(36)-C(37)-Cl(8)	121.0(3)
C(32)-O(3)-H(3)	116(3)	C(33)-O(4)-H(4)	111(3)
O(3)...O(2)	2.642(6)	H(3)...O(2)	1.68(5)
O(3)-H(3)...O(2)	171(5)		
O(4)...O(2)	2.626(5)	H(4)...O(2)	1.67(2)
O(4)-H(4)...O(2)	170(5)		

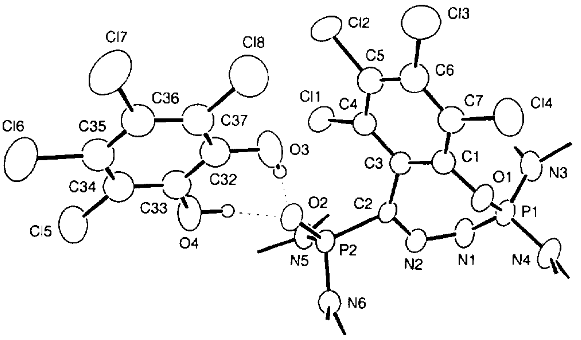
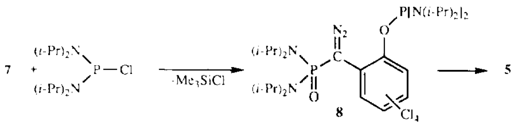


Fig 2. Ortep drawing and numbering scheme for **5**.

Compound **5** features a seven-membered heterocycle and the P=O group is complexed to a catechol unit. Obviously, the formation of this product was not expected but can be easily rationalized. When monitoring the reaction by ^{31}P NMR spectroscopy a signal corresponding to the bis(diisopropylamino)chlorophosphine was detected after a few minutes. This is due to the presence of HCl in the commercially available tetrachloro-*ortho*-benzoquinone which decomposes the starting diazophosphine **1**. Thus, it is quite possible that the chlorophosphine reacts with the silyloxy derivative **7**, giving trimethylchlorosilane and diazo compound **8**, which then undergoes an intramolecular Staudinger Meyer reaction [6] (scheme 5).



Scheme 5

Conclusion

These results clearly demonstrate the high instability of diazomethylenephosphoranes. The synthesis of a halogen-free diazomethylenephosphorane, which would constitute a very powerful building block, remains a difficult challenge.

Experimental section

General

All experiments were performed under a dry argon atmosphere. Melting points were obtained on a electrothermal capillary apparatus and were not corrected. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on Bruker AC80, AC200 or WM250 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P downfield shifts are expressed with a positive sign in ppm relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1725X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

Addition of tetrachloro-1,2-benzoquinone to [bis(diisopropylamino)phosphino]trimethyl)silyldiazomethane

To a THF solution (15 mL) of diazo derivative **1** (0.50 g, 1.45 mmol) at −78°C was added a THF solution (10 mL) of TCBQ (0.36 g, 1.45 mmol). After warming to room temperature the solvent was removed under vacuum, and the residue was filtered on silica gel.

Oxophosphoranyldiazo derivative 4

Yellow crystals. R_f = 0.3, pentane/Et_2O (95:5). Yield: 30%; mp 130°C dec.

^{31}P NMR ($CDCl_3$) δ + 32.6 ppm.

^{1}H NMR ($CDCl_3$) δ 1.13 (d, J(HH) = 6.6 Hz, 12H, CH_3), 1.32 (d, J(HH) = 6.6 Hz, 12H, CH_3), 3.52 (sept d, J(HH) = 6.6 Hz, J(PH) = 18.5 Hz, 4H, CH).

^{13}C NMR ($CDCl_3$) δ 22.8 and 22.9 (s, CH_3), 47.5 (d, J(PC) = 5.6 Hz, CH), 51.2 (d, J(PC) = 196.4 Hz, CN_2), 114.2 (d, J(PC) = 5.4 Hz, C_2), 116.2 (s, C_4), 122.5 (d, J(PC) = 22.1 Hz, C_7), 132.3 (d, J(PC) = 4.5 Hz, C_6), 133.4 (s, C_5), 162.8 (s, C_3).

IR (CH_2Cl_2) 2 082 cm^{-1} (νCN_2).

Mass spectrum m/z 518 (M^+).

Anal calc for $C_{19}H_{29}N_4O_2PCl_4$: C, 44.03; H, 5.60; N, 10.81. Found: C, 44.01; H, 5.63; N, 10.30.

2,2-Bis(diisopropylamino)-5-{[bis(diisopropylamino)-phosphinyl]diazomethyl}-6,7,8,9-tetrachloro-1,3,4,2λ⁵-benzoxadiazaphosphepine 5

Yellow crystals. R_f = 0.7 (Et_2O). Yield 5%; mp 175°C.

^{31}P NMR ($CDCl_3$) δ + 19.6 (d, J(PP) = 2.8 Hz), + 21.5 (d, J(PP) = 2.8 Hz) ppm.

^{1}H NMR ($CDCl_3$) δ 0.79 (d, J(HH) = 6.7 Hz, 6H, CH_3), 1.12 (d, J(HH) = 6.7 Hz, 6H, CH_3), 1.18 (d, J(HH) = 6.7 Hz, 6H, CH_3), 1.22 (d, J(HH) = 6.7 Hz, 6H, CH_3), 1.38 (d, J(HH) = 6.6 Hz, 12H, CH_3), 1.41 (d, J(HH) = 6.9 Hz, 12H, CH_3), 3.60 (sept d, J(HH) = 6.7 Hz, J(PH) = 17.3 Hz, 4H), 3.88 (sept d, J(HH) = 6.6 Hz, J(PH) = 16.8 Hz, 2H), 4.21 (sept d, J(HH) = 6.9 Hz, J(PH) = 11.7 Hz, 2H, CH), 8.97 (s, 2H, OH).

^{13}C NMR ($CDCl_3$) δ 21.8 (d, J(PC) = 1.4 Hz, CH_3), 22.5 (d, J(PC) = 1.2 Hz, CH_3), 22.9 (d, J(PC) = 2.7 Hz, CH_3), 23.2 (s, CH_3), 23.3 (s, CH_3), 23.5 (s, CH_3), 23.9 (d, J(PC) = 1.4 Hz, CH_3), 24.6 (d, J(PC) = 1.6 Hz, CH_3), 46.1 (d, J(PC) = 5.4 Hz, CH), 47.3 (d, J(PC) = 4.8 Hz, CH), 47.6 (d, J(PC) = 4.5 Hz, CH), 47.9 (d, J(PC) = 6.2 Hz, CH), 119.7 (s, *C*C-OH), 121.9 (s, *C*CC-OH), 125.2 (d, J(PC) = 5.8 Hz, C_6), 126.4 and 126.8 (s, C_4 and C_5), 131.2 (d, J(PC) = 84.9 Hz, C_2), 132.8 (d,J(PC) = 81.4 Hz, C_3), 142.3 (s, C-OH), 145.6 (t,J(PC) = 5.9 Hz, C_1), 154.3 (dd,J(PC) = 194.9 and 20.3 Hz, C=N).

Anal calc for $C_{37}H_{58}N_6O_4P_2Cl_8$: C, 44.60; H, 5.87; N, 8.43. Found: C, 43.88; H, 5.98; N, 7.99.

Crystal structure analysis of 4

$C_{19}H_{29}Cl_4N_4O_2P$, M = 518.25, yellow parallelepiped obtained by recrystallization from dichloromethane, crystal dimensions 0.55 × 0.35 × 0.30 mm, monoclinic, space group $P2_1/n$ (No 14): a = 8.220(1) Å, b = 20.105(2) Å, c = 15.407(2) Å, β = 102.34(2)°, V = 2 487.4(8) $Å^3$, Z = 4, $F(000)$ = 1 080, D_c = 1.384 $g.cm^{-3}$, μ

(Mo$K\alpha$) = 0.56 mm^{-1}; 5 778 reflections were collected on a Enraf-Nonius CAD4 diffractometer ($2\theta_{max}$ = 54°). Of these, 3 651 reflections with $F_0^2 > 3\sigma(F_0^2)$ were used for the solution (direct methods, SHELXS-86)[13] and refinement (full-matrix least-squares using SHELX76)[14]. All non-H atoms were anisotropic. H atoms were found on a difference Fourier map; those bonded to C atoms were introduced in calculations in constrained geometry (C-H = 0.97 Å), with isotropic thermal parameters first refined, then kept fixed to 0.08 Å^2 for the methyls and to 0.06 Å^2 for others. The H atom bonded to O(2) was allowed to vary. Scattering factors (f', f'') were taken from *International Tables for X-ray Crystallography.* Last full-matrix refinement cycle: $R(F_0)$ = 0.032, R_w = 0.031 with unit weights, 3 651 observations, 275 variable parameters, S = 0.883, max parameter shift/esd = 0.009, max and min residual peaks of 0.25 and −0.24e/Å^3.

Crystal structure analysis of 5

$C_{37.5}H_{59}Cl_9N_6O_4P_2$, M = 1 038.94, yellow parallelepiped obtained by recrystallization from dichloromethane, crystal dimensions 0.50 × 0.35 × 0.15 mm, triclinic, space group $P\bar{1}$(No 2): a = 12.996(1) Å, b = 20.746(2) Å, c = 10.028(1) Å, α = 92.87(1)°, β = 101.91(1)°, γ = 107.94(1)°, V = 2 498.1(5)Å^3, Z = 2, F(000) = 1 082, D_c = 1.381 g.cm^{-3}, μ (Mo$K\alpha$) = 0.61 mm^{-1}: 6 994 reflections were collected on a Enraf-Nonius CAD4 diffractometer ($2\theta_{max}$ = 46°). Of these, 4 014 reflections with $F_0^2 > 3\sigma(F_0^2)$ were used for the solution (direct methods, SHELXS-86)[13] and refinement (full-matrix least-squares using SHELX76)[14]. All non-H atoms were anisotropic, except phenyl rings refined as isotropic rigid groups (C-C = 1.395 Å) and solvent atoms. H atoms were found on a difference Fourier map, those bonded to C atoms were introduced in calculations in constrained geometry (C-H) = 0.97 Å), with isotropic thermal parameters first refined, then kept fixed to 0.10 Å^2 for methyls and to 0.06 Å^2 for others. The H atoms bonded to O(3) and O(4) were allowed to vary with a fixed U_{iso} equal to 0.07 Å^2. Scattering factors (f', f'') were taken from *International Tables for X-ray Crystallography.* Last full-matrix refinement cycle: $R(F_0)$ = 0.044, R_w = 0.046 with unit weights, 4 014 observations, 448 variable parameters, S = 1.119, max parameter shift/esd = 0.218 (a solvent parameter), max and min residual peaks of 0.67 and −0.56 e/Å^3.

Supplementary material

Supplementary material data (structure factors for compounds **4** and **5**) have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° = SUP 90397 and is available on request from the Document Supply Center.

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