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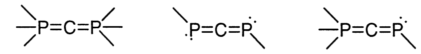
Synthesis, Structure, and Reactivity of a $1\sigma^4,3\sigma^2$-Diphosphaallene**

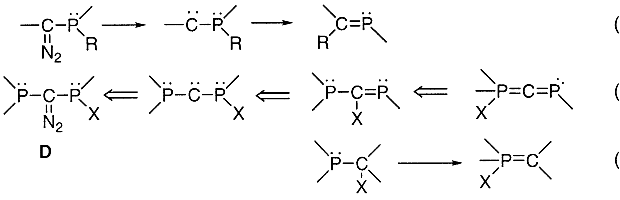
Tsuyoshi Kato, Heinz Gornitzka, Antoine Baceiredo, and Guy Bertrand*

Among the possible heterocumulenes featuring the PCP sequence, $1\sigma^4,3\sigma^4$-diphosphaallenes (carbodiphosphoranes) **A**[1] and $1\sigma^2,3\sigma^2$-diphosphaallenes **B**[2] have been known for many years. Here we report the synthesis of a $1\sigma^4,3\sigma^2$-diphosphaallene **C**. Such a highly functionalized molecule (two different types of phosphorus–carbon "double" bond and a lone pair at one of the phosphorus atoms) has only been postulated as an intermediate, but never observed spectroscopically.[3]



A **B** **C**

Our synthetic strategy was based on two consecutive rearrangements: the well-established 1,2-migration reaction of singlet carbenes,[4] which operates for phosphinocarbenes [Eq. (1)],[5] and the 1,2-halogen shift associated with α-halogenophosphanes [Eq. (3)].[6] Combining these two 1,2-migration reactions, a possible precursor for the preparation of the desired $1\sigma^4,3\sigma^2$-diphosphaallene can be identified as the (phosphino)(chlorophosphino)diazomethane of type **D** [Eq. (2)].

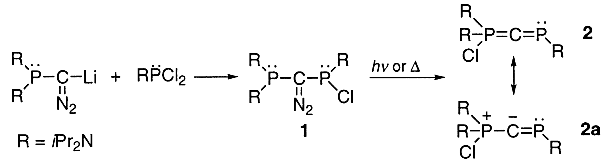


(1)

(2)

(3)

Exactly this type of derivative, namely [bis(diisopropylamino)phosphino][chloro(diisopropylamino)phosphino]diazomethane (**1**), is readily available in one step by addition of the lithium salt of [bis(diisopropylamino)phosphino]diazomethane[7] to dichloro(diisopropylamino)phosphane (Scheme 1).



Scheme 1.

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The photolysis (300 nm) or thermolysis (70 °C) of a solution of the diazo derivative **1** in toluene leads to the formation of the cumulene **2**, as only one isomer, in near quantitative yield (according to ^{31}P NMR spectroscopy).

The ^{31}P{^{1}H} NMR spectrum of **2** showed two doublets at $\delta = 302.8$ and 61.2 (^2J(P,P) = 240.1 Hz) in the regions expected for a σ^2- and a σ^4-phosphorus atom, respectively.[8] The signal for the dicoordinate carbon atom appears as a doublet of doublets at $\delta = 169.9$ (^1J(P,C) = 36.5, 9.7 Hz), with a chemical shift approximately halfway between the values observed for carbodiphosphoranes **A** and diphosphaallenes **B**.[9] The molecular structure of **2** was unambiguously established by an X-ray diffraction study (Figure 1).[10] The C1–P1 bond length (1.64 Å) is markedly shorter than an isolated C=P bond,[11] but comparable with the value observed for a diphosphaallene of type **B**.[2] The planarity of the N1-P1-C1-P2-Cl1 fragment (maximum deviation 0.0169 Å) and the value of the P1-C1-P2 angle of 120.88° are in agreement with an sp^2-hybridized carbon atom. As expected, the molecule has an *E* configuration. The presence of a lone pair of electrons at C1 (form **2a**; Scheme 1) interacting with P2 is confirmed by the short P2–C1 bond length (1.65 Å) and the P2–Cl1 bond in an eclipsed position to the C1-P1-N1 fragment. This so-called negative hyperconjugation[12] transfers the electron density from the occupied sp^2 orbital on the C1 atom to the energetically low-lying σ* orbital of the P2–Cl1 bond.[13] Therefore, derivative **2** can be considered as an heterocumulene (Scheme 1).

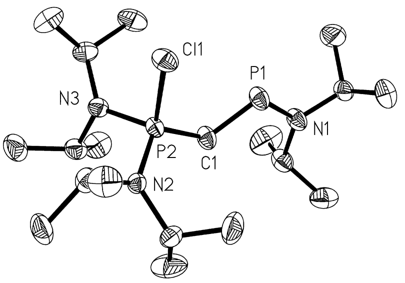
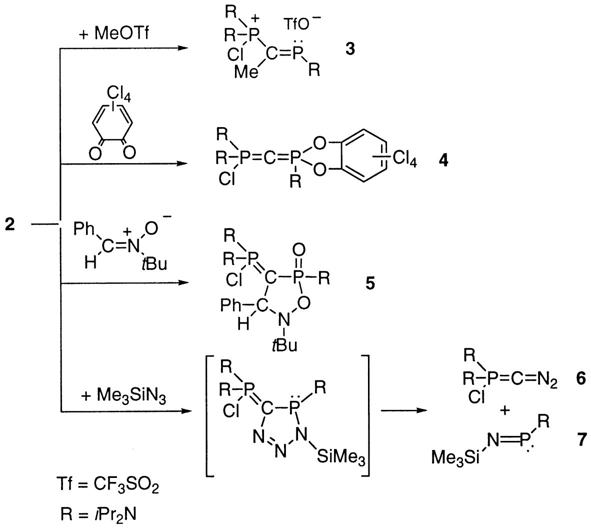


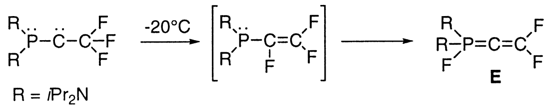
Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: C1-P1 1.6429(13), C1-P2 1.6503(13), P1-N1 1.6707(11), P2-N2 1.6393(11), P2-N3 1.6627(11), P2-Cl1 2.1267(4); C1-P1-N1 108.05(6), P1-C1-P2 120.88(9), C1-P2-Cl1 115.99(5), C1-P2-N2 113.91(6), C1-P2-N3 116.48(7).

Derivative **2** is a versatile and selective reagent as illustrated by the reactions given in Scheme 2. Owing to the presence of an ylidic carbon atom, **2** reacts with an alkylating agent such as methyl trifluoromethanesulfonate to give the expected C-phosphoniophosphaalkene **3** as only one isomer (59 % yield).[14] The lone pair of electrons at the phosphorus center can be used for a formal [1+4] cycloaddition with tetrachloro-*o*-benzoquinone to afford the carbodiphosphorane **4**, which was isolated in 62 % yield. Note that the alternative [2+4] cycloadduct involving the P=C bond was not observed.[15] However, the phosphorus–carbon π bond remains an excellent dipolarophile as shown by the reaction with a nitrone. Heterocycle **5**, resulting from a diastereoselective [2+3] cycloaddition, followed by a subsequent oxidation by the excess of nitrone, was isolated in 85 % yield and fully characterized both spectroscopically and by a single-crystal X-ray diffraction study.[9b)] A [3+2] cycloaddition reaction also occurs with trimethylsilyl azide, but the resulting adduct fragments cleanly into the iminophosphane **6** and the diazomethylenephosphorane **7**.[16] This is an attractive synthetic route for this very unique stable diazocumulene.[17]



Scheme 2.

The formation of the 1σ^4,3σ^2-diphosphaallene **2** from **1**, along with the recently described synthesis of the σ^4-phosphaallene **E** [Eq. (4)],[18] strongly suggest that the sequence of two successive 1,2-halogen migrations should become a general route for the preparation of a variety of hitherto unknown heterocumulenes featuring a σ^4-phosphorus center.



(4)

Experimental Section

All operations were carried out under argon using Schlenk tube techniques.

1: A solution of dichloro(diisopropylamino)phosphane (3.10 g, 15.3 mmol) in THF (20 mL) was added to a solution of the lithium salt of [bis(diisopropylamino)phosphino]diazomethane[7] (15.3 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to warm to 0 °C over a period of 1 h. After evaporation of the solvent under vacuum at 0 °C, the residue was quickly extracted with pentane (20 mL) and filtered. After the volume of solvent had been reduced to 5 mL, orange crystals of **1** (4.02 g, 60 %) were obtained at −20 °C; m.p. 30 °C (decomp). ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 110.6$, 59.0 (d, ^2J(P,P) = 239.6 Hz); IR (pentane): $\tilde{\nu} = 2039$ cm^{-1} (CN_2).

2: A solution of the diazo derivative **1** (0.044 g, 0.1 mmol) in toluene (1 mL) was heated at 70 °C for 4 h. ^{31}P NMR spectroscopy indicated the quantitative formation of **2**. After evaporation of the solvent, **2** was obtained as pale yellow crystals from a saturated pentane solution at 0 °C (0.037 g, 90 %); m.p. 73–74 °C.

The experiments used to prepare **3**–**5** were performed with a solution of freshly prepared cumulene **2** (0.041 g, 0.1 mmol) in pentane or toluene (1 mL).

3: Methyl trifluoromethanesulfonate was added to a solution of **2** at −78 °C and the alkylated compound **3** precipitated as a white powder from the solution mixture (0.034 g, 59 %); m.p. 136–137°C. ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 309.7$, 79.9 (d, ^2J(P,P) = 192.5 Hz); ^{1}H NMR (CDCl$_3$): $\delta = 2.23$ (dd, ^3J(P,H) = 6.8, 23.0 Hz, 3H; C-CH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 18.8$ (dd, ^2J(P,C) = 3.4, 3.7 Hz, C-CH$_3$), 109.7 (dd, ^1J(P,C) = 131.3, 64.5 Hz, PCP).

4: Tetrachloro-*o*-benzoquinone was added to a solution of **2** at −78°C and the resulting carbodiphosphorane **4** was crystallized from a toluene/pentane solution at −20°C as white crystals (0.031 g, 48 %); m.p. 143–144°C. ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta = 25.5$, 21.5 (d, ^2J(P,P) = 126.4 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 38.3$ (dd, ^1J(P,C) = 149.4, 187.2 Hz, P=C=P).

5: The nitrone Ph(H)C=N(O)*t*Bu was added to a solution of **2** at room temperature and the solution was heated at 55°C for 15 days. The cycloadduct **5** precipitated from an Et$_2$O/CH$_3$CN solution at −20°C as colorless crystals (0.051 g, 85 %); m.p. 160–161°C. ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 71.0$, 46.8 (d, ^2J(P,P) = 67.8 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 40.0$ (dd, ^1J(P,C) = 131.4, 17.5 Hz, P-C-P), 72.2 (dd, ^2J(P,C) = 14.7, 6.4 Hz, Ph-C-H).

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4,5-Bis(diphenylphosphinoyl)-1,2,3-triazole: A Powerful New Ligand That Uses Two Different Modes of Chelation

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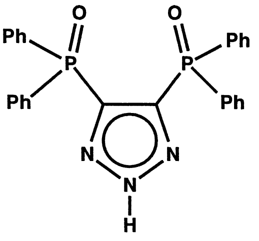
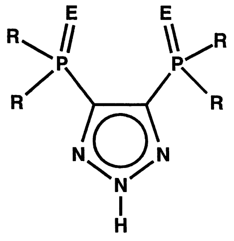
We report a novel and powerful ligand that is thermally, oxidatively, and hydrolytically very stable. It avidly forms complexes with cations through the adoption of two entirely different chelation modes, allowing the facile extraction of metal ions from aqueous systems. This novel ligand is the anion [L^T]$^-$ of 4,5-bis(diphenylphosphinoyl)-1,2,3-triazole L^{T}H, which combines the features of the coordinating ability of the P(O)Ph$_2$ groups with the nitrogen donor atoms of the triazole ring. Moreover, it is the prototype of a much broader family of ligands with the general structure L^X, in which E can



L^{T}H



L^X

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