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1,2λ^5,5λ^5-Azadiphospholium Structures

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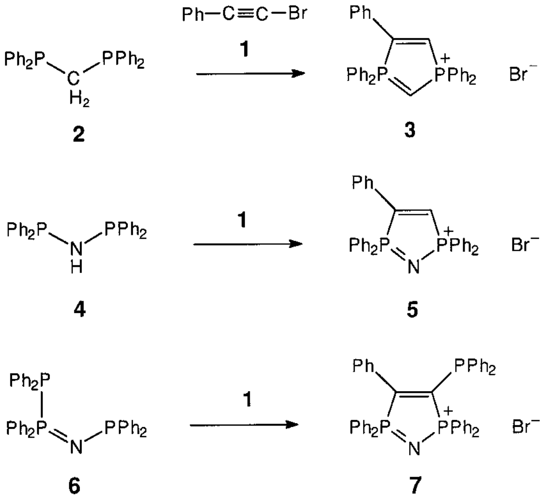
ABSTRACT

The reactions of bromophenylacetylene with the diphenylphosphino amines $(Ph_2P)_2NH$ *and* $(Ph_2P)_3N$ *result in the 1,1,3,3,4-pentaphenyl-1,2,5-azadiphospholium bromide (***5***) and its 4-diphenylphosphino derivative (***7***). Their X-ray structure analyses show planar rings for the cations. The small endocyclic angle at the nitrogen ring member is associated with PN bonds that are longer than in the acyclic cation* $(Ph_3P)_2N^+$*. The data fit to a negative linear relationship of PN bond lengths and PNP bond angles.*

The reactions of bromophenylacetylene **1** with bis(diphenylphosphino)methane **2** and bis(diphenylphosphino)amine **4** provide an easy access to 1,1,3,3,4-pentaphenyl-1,3-diphospholium bromide **3** and 2,2,3,5,5-pentaphenyl-1,2,5-azadiphospholium bromide **5** [1,2]. The analogous reaction with the tetraphenyldiphosphine diphenylphosphinoimine **6**, which is a more stable isomer [3] than tris(diphenylphosphino)amine $(Ph_2P)_3N$, results in the formation of 4-diphenylphosphino-2,2,3,5,5-pentaphenyl-1,2,5-azadiphospholium bromide **7**. The pathway leading to these products has been discussed [2]. The cations of **5** and **7** challenge a structural comparison with related open chain cations (see Scheme 1).



SCHEME 1

TABLE 1 Selected Bond Lengths (pm) and Bond Angles (°) of the 1,2,5-Azadiphospholium Ions **5** and **7**

	5	**7**
P1–N1	160.0(3)	160.9(4)
P2–N1	160.4(3)	160.0(4)
P1–C1	178.7(3)	184.0(5)
P2–C2	184.0(3)	183.6(5)
C1–C2	133.6(5)	136.0(7)
P3–C1		183.2(5)
P1–N1–P2	111.6(2)	111.8(2)
N1–P1–C1	103.0(2)	103.1(2)
N1–P2–C2	102.9(2)	103.5(2)
P1–C1–C2	113.3(3)	110.7(4)
P2–C2–C1	109.1(3)	110.7(4)
P1–C1–P3		115.7(3)
C2–C1–P3		133.3(4)

Dedicated to Professor Robert W. Parry on the occasion of his eightieth birthday.

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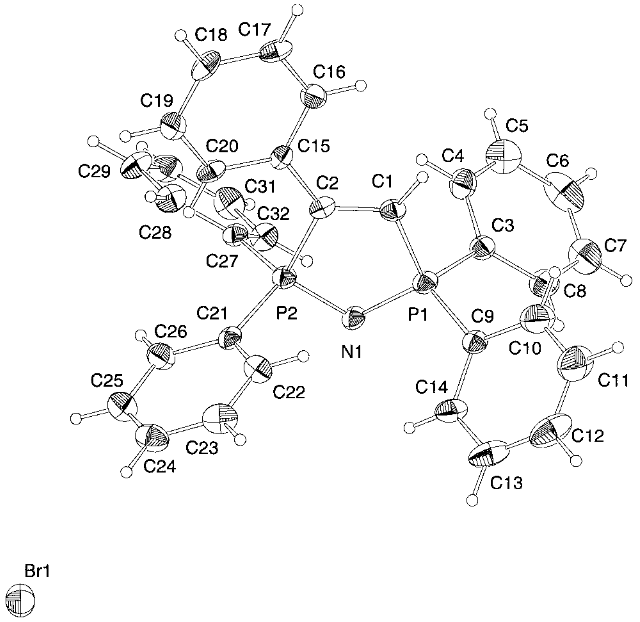

FIGURE 1 Molecular structure of **5** in the crystal (thermal ellipsoids with 30% probability).

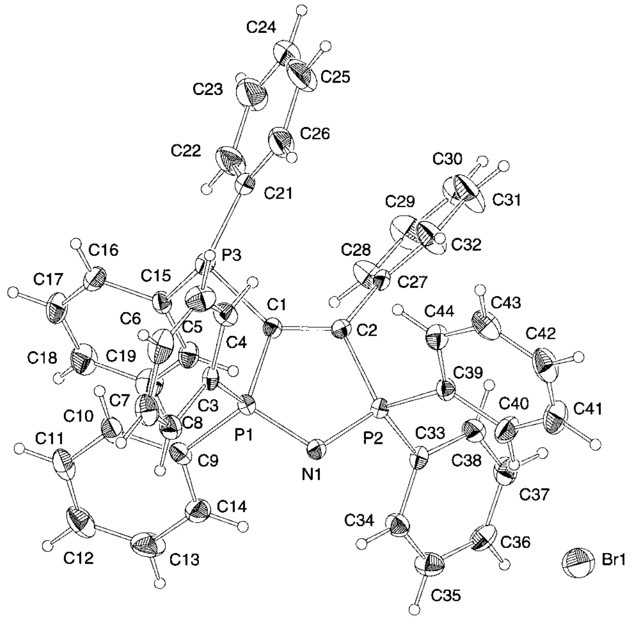

FIGURE 2 Molecular structure of **7** in the crystal (thermal ellipsoids with 30% probability).

TABLE 2 Crystal Data and Structure Refinement

	5	**7**
Empirical formula	$C_{32}H_{26}BrNP_2$	$C_{44}H_{35}BrNP_3$
M	566.39	750.55 g mol^{-1}
T	293(2)	293(2) K
λ	0.71073	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	C2/c	P21/n
a	22.984(4)	12.731(1) Å
b	14.682(2)	22.852(7) Å
c	19.769(4)	12.909(1) Å
β	124.097(13)	97.459(7)°
V	5524(2)	3723.9(12) Å^3
Z	8	4
d (calcd.)	1.362	1.339 Mg m^{-3}
μ	1.625	1.265 mm^{-1}
F(000)	2320	1544
Crystal size	0.57 × 0.53 × 0.33	0.63 × 0.53 × 0.27 mm
θ range	2.47–22.98	2.39–23.00°
Index ranges	$-25 \leq h \leq 20$	$-13 \leq h \leq 13$
	$-16 \leq k \leq 0$	$0 \leq k \leq 25$
	$0 \leq l \leq 21$	$0 \leq l \leq 14$
Reflections collected	3954	5427
Independent reflections	3821 [R(int) = 0.0213]	5167 [R(int) = 0.0297]
Observed reflections [$I > 2\sigma(I)$]	2784	4083
Absorption correction	semiempirical from Ψ-scans	
max./min. transmission	0.9997/0.7948	0.9997/0.8336
Refinement method	full-matrix least-squares on F^2	
Data/restraints/parameters	2784/0/325	4083/0/442
Goodness-of-fit on F^2	1.103	1.017
Final *R* indices *R*1	0.0411	0.0622
[$I > 2\sigma(I)$] *wR*2	0.0938	0.1813
R indices *R*1	0.0641	0.0795
(all data) *wR*2	0.1080	0.1975
Largest diff. peak/hole	0.259/−0.408	0.491/−1.116 e Å^{-3}

The result of single-crystal structure analyses of **5** and **7** confirm their ionic structures (Figures 1 and 2). In the cations, the ring atoms and the ligand atoms at C1 and C2 are coplanar. The endocyclic angles at the tetrahedral phosphorus atoms are smaller (103–104°C), and those at the (Ψ-)trigonal members are larger (109–113°C) than in a regular pentagon (Table 1).

The PNP unit in the cations both of **5** and **7** is symmetric with a bond angle of 112° and an average bond length of 160.3 pm. It may be compared to the acyclic bis(triphenylphosphine)iminium cation $Ph_3P=N-PPh_3^+$. As this cation is frequently used to crystallize salts of anionic complexes, many structural determinations of it are available [4]. They have shown the cation in most of the salts to have a bent geometry with a PNP angle in the range 135°–142° and PN bond lengths in the region of 156.6–158.6 pm. In one case, a linear PNP array has been found with rather shorter PN bonds (153.9 pm) than in the bent form. Our new results complement these findings in the sense of a linear relationship: the smaller the PNP angle, the longer the PN bonds [5].

The substitution of C1 in **5** by a diphenylphosphino group to give **7** results in a slight decrease of the endocyclic angle at C1 from 113° to 111° and in an elongation of the adjacent CC bond (134 → 136 pm) and the adjacent CP bond (179 → 184 pm).

For the X-ray structure analyses, an ENRAF-NONIUS CAD4 diffractometer was used. Details are given in Table 2. Additional information of the crystal structure determination are deposited at the Cambridge Crystallographic Data Center (CCDC) and may be requested by quoting the name of the authors and the journal citation.

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[5] This relationship is paralleled by the long-known PN bond contraction evident in the change from cyclotriphosphazenes to higher cyclic homologues that generally is accomplished by an increase in the PNP bond angle. H. R. Allcock: *Phosphorus-Nitrogen Compounds,* Academic, New York, p. 36 (1972).