Heteroatom Chemistry
Volume 2, Number 5, 1991

$1\lambda^5,3\lambda^5$-Diphospholium Ions†

Alfred Schmidpeter,* Peter Mayer, and Johanna Stocker

Institut für Anorganische Chemie der Universität, Meiserstrasse 1, D-8000 München 2, Germany

Kenneth A. Roberts and Peter J. Stang

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Received 15 July 1991.

ABSTRACT

One example each is given for the reaction of bromoacetylenes and ethynyl-phenyliodonium tosylates with bis(diphenyl phosphino)methane. The yellow crystalline 1:1-addition products are diphospholium salts. They readily and selectively hydrolyze to give 2-phosphinoylethenyl phosphonium salts.

INTRODUCTION

The units CR and PR_2 both provide three electrons for further bonding. R_2P can thus formally replace RC in a delocalized carbocyclic system. The character of the bonding will be different, however [1]. While the overall charge of the system will be unchanged, the electron density at the carbon members adjacent in the ring to the phosphorus will strongly increase because the PC bonds in the ring are ylidic in character. Examples of such ring systems derived from benzene are the λ^5-phosphinines (**1**) [2,3], $1\lambda^5,3\lambda^5$-diphosphinines (**2**) [4–6], and $1\lambda^5,4\lambda^5$-diphosphinines (**3**) [7,8]. The $1\lambda^5,3\lambda^5,5\lambda^5$-triphosphinines (**4**) recently reported are the only representatives known [9]; such structures probably suffer from the accumulation of carbanion-type members in the ring. Conversely, electron-deficient carbocyclic systems could benefit from the CR/PR_2 exchange. In this sense, the λ^5-phospholium ions (**5**) and the $1\lambda^5,3\lambda^5$-diphospholium ions (**6**) may be viewed from an energy viewpoint as favored derivatives of the antiaromatic cyclopentadienyl cation [10] (Scheme 1).

λ^5-Phospholium ions **5** have been prepared by alkylation or acylation of phospholes [11,12], but of the $1\lambda^5,3\lambda^5$-diphospholium ions, only benzoderivatives **7** [13] seem to be known. A recently reported aza-diphosphafulvene [14] is closely related to **6** as can best be seen from its zwitterionic formula **8** (R = NMe_2, X = NPh). We now find that diphospholium ions **6** are readily obtained from the reaction of a diphosphinomethane and a bromoacetylene or an alkynyl-phenyliodonium tosylate [15].

PREPARATION

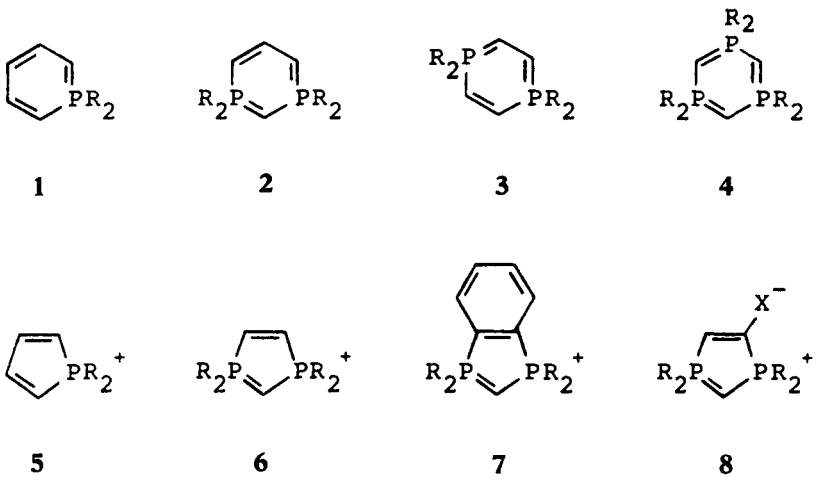
Bis(diphenylphosphino)methane added phenylbromoethyne at room temperature in a clean reaction to give pentaphenyl-1,3-diphospholium bromide **6a**. The 4-*tert*-butyl derivative **6b** was formed in the reaction with the respective phenyl(ethynyl)iodonium tosylate (Reaction 1). As a first step, the reaction most likely involves the formation of an alkynylphosphonium ion. An intramolecular nucleophilic attack of the remaining phosphino group onto the carbon β to the phosphonium center and a subsequent 1,3-proton shift will complete the reaction. For both steps, independent model reactions are well known; haloalkynes and tertiary phosphines yield alkynylphosphonium halides [16–18], and the mechanism of this reaction and possible side reactions have been discussed [19]. An ethynylphenyliodonium tosylate gives the respective phosphonium salt quantitatively (see Experimental). Furthermore, the hydrobromide of triphenylphos-

This paper is dedicated to Professor Dr. Leopold Horner on the occasion of his eightieth birthday.

*To whom correspondence should be addressed.

†Four- and Five-membered Phosphorus Heterocycles, Part 79. Part 78: I. A. Litvinov, K. Karaghiosoff, A. Schmidpeter, E. Ya. Zabotina, E. N. Dianova, *Heteroatom Chem. 2*, 1991, 369.

1042-7163/92/$3.50 + .25



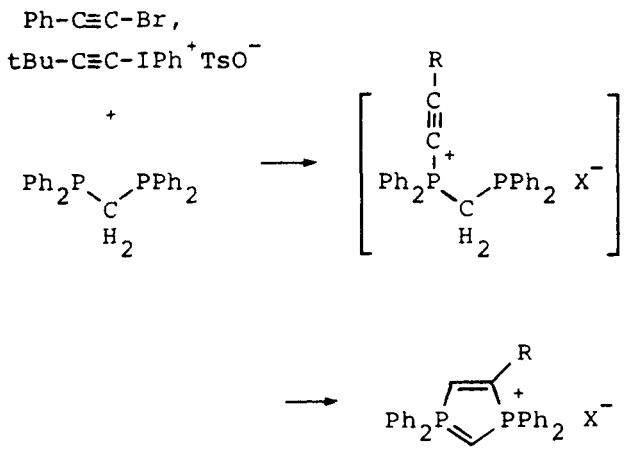
SCHEME 1

phine adds readily to the triple bond of the phenylethynyl-triphenylphosphonium cation [18].

In the above reaction the ethynylphosphonium stage obviously is passed too rapidly to be identified for certain. During the formation of **6a** an AX system was observed in the ^{31}P NMR spectra (δ_A = 29.5, δ_X = −28.0, J_{AX} = 51.1 Hz), which fits well with the suggested intermediate, but which never gained more than 2% intensity.

The diphospholium salts **6a,b** are yellow crystalline compounds. Their identity follows beyond doubt from the NMR spectra (Tables 1 and 2). The high field chemical shifts of 2-H and C-2 reflect the ylidic nature of this unit. These data may be compared to those of the benzo derivatives **7** (δ^1H = 1.4 to 2.3, $^2J_{PH}$ = 9 to 10 Hz; $\delta^{13}C$ = −4.4 to −4.7, $^1J_{PC}$ = 114 to 115 Hz) [13].

The isomerization of the initial alkynylphosphonium ion to the diphospholium ring is also accompanied by a change in reactivity. Whereas alkynylphosphonium salts are rather stable to hydrolysis [18], the diphospholium salts, because of their ylidic nature, are expected to hydrolyze readily. The compounds **6a,b** were indeed very sensitive to water and in solution they hydrolyzed rapidly when exposed to moist air. This reaction could be monitored by ^{31}P NMR spectroscopy and could also be followed by the fading of the yellow color.



6a R = Ph, X = Br

6b R = tBu, X = TsO

REACTION 1

HYDROLYSIS

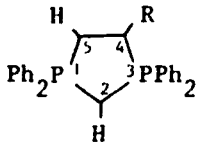
Hydrolysis will cleave one of the PC bonds of **6** and open the ring. For this there is a choice of two types of PC bonds, the 1,2 and 3,2 bonds of the PCP unit or the 1,5 and 3,4 bonds. Whereas the hydrolysis of a 4*H*-1λ⁵,3λ⁵-diphosphole cleaved both of the latter and preserved the PCP unit [21], hydrolysis of **6** exclusively opened one of the former to yield the (*z*)-2-phosphinoylethenylphosphonium salts **9,10.** The hydrolytic cleavage of the 1,2 bond has also been

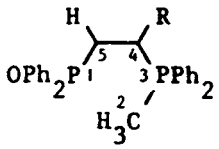
TABLE 1 ^{31}P *NMR Data of* **6a,b, 9a,b** *and* **10a** *(in* $CDCl_3$*)*[a]

R	**6a** Ph	**6b** *t*Bu	**9a** Ph	**9b** *t*Bu	**10a** Ph
δ P-1	34.3	30.7	21.8	22.0	15.6
δ P-3	40.5	43.9	23.5	23.9	28.4
J_{PP} (Hz)	72.2	73.6	14.8	14.6	13.7

[a] The signals of **6a** and **9a** are assigned to P-1 and P-3 (see Table 2) with the help of ^1H coupled spectra, those of the other compounds by analogy.

TABLE 2 *^1H and ^{13}C NMR Data of* **6a** *and* **9a,b**[a] *(in $CDCl_3$)*



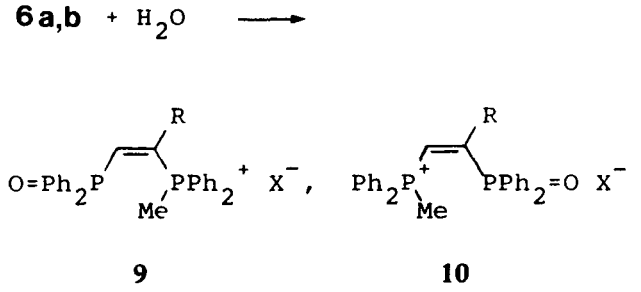


		6a		9a		9b		
	δ 2-H	2.0	ddd	3.4	d	3.4	d	
	$^2J_{PH}$	12.0		13.9		14.7		
	$^2J_{PH}$	8.7						
	δ 5-H	8.8	ddd	7.5[b]		[b]		
	$^2J_{PH}$	22.9						
	$^3J_{PH}$	42.6						
	$^4J_{HH}$	2.1						
	δ C-2	−3.1	t	13.8	d	14.1	d	
	$^1J_{PC}$	113.5		55.1		53.6		(130.7)
	δ C-4	151.2	dd	144.3	dd	153.0	dd	
	$^1J_{PC}$	78.2		70.3		59.5		
	$^2J_{PC}$	10.4		1.6		5.5		
	δ C-5	133.0	dd	146.9	dd	140.1	dd	
	$^1J_{PC}$	86.4		84.7		86.2		(149.3)
	$^2J_{PC}$	15.6		9.7		10.0		
1-Ph	δ C-*i*	126.3[c]	dd	d		131.0	d	
	$^1J_{PC}$	91.8				109.0		
	$^3J_{PC}$	2.8						
	δ C-*o*	132.2[c]	d	131.3[c]	d	130.7[a]	d	
	$^2J_{PC}$	11.4		10.5		10.0		(162.5, 7.9, 7.9)
	δ C-*m*	129.6[c]	d	129.3[c]	d	129.2[a]	d	
	$^3J_{PC}$	12.8		12.6		12.3		(163.5, 6.6)
	δ C-*p*	133.8[c]	d	132.8	d	132.3	d	
	$^4J_{PC}$	3.3		2.6		2.8		(161.1, 6.9)
3-Ph	δ C-*i*	125.5[c]	dd	120.8	d	122.7	d	
	$^1J_{PC}$	87.4		88.1		85.8		(9.9)
	$^3J_{PC}$	3.4						
	δ C-*o*	132.0[c]	d	133.2[c]	d	133.7[a]	d	
	$^2J_{PC}$	11.9		10.5		10.9		(164.4, 8.8, 6.9)
	δ C-*m*	129.5[c]	d	129.4[c]	d	129.5[a]	d	
	$^3J_{PC}$	13.3		13.6		12.8		(165.4, 7.6)
	δ C-*p*	133.3[c]	d	134.0	d	134.0	d	
	$^4J_{PC}$	2.9		3.2		3.3		(164.0, 6.6)
4-R	δ C-*i*	131.9	dd	137.6	dd	42.7	dd	
	$^2J_{PC}$	11.4		10.2		9.5		
	$^3J_{PC}$	17.1		14.0		11.4		
	δ C-*o*	128.3	d	d		30.3	d	
	$^3J_{PC}$	4.3				3.3		(127.9)
	δ C-*m*	129.1	s	d				
	δ C-*p*	131.9	s	d				

[a] In parentheses for **9b** are given $^1J_{CH}$ (Hz).
[b] Signal superimposed by signals of phenylprotons, for **9a** from ^1H NOESY.
[c] Signals tentatively assigned to 1-Ph and 3-Ph; for C-*i,p* in **9** the assignment is based on a comparison with known data [20].
[d] Signal not identified.

observed for the benzo derivatives **7** followed by that of the 3,4 bond [13] (Reaction 2). In **6a,b** the two PC bonds of the PCP unit are inequivalent because of the substituent R in the 4 position, and hydrolysis can thus lead to two isomeric products **9** and **10**. It was found to be remarkably regio selective in this respect; in the case of R = Ph a 24:1 ratio of **9a:10a** resulted, and in the case of R = *t*Bu no sign of **10b** was observed. The products **9** were isolated as colorless crystalline material.

The ^{31}P NMR spectra of compounds **9** and **10** displayed AB systems (Table 1). Their chemical shifts were in accord with the suggested structures: While the difference δ P-3 − δ P-1 originating from R in



9 10

REACTION 2

6 is essentially compensated in **9** by the usual downfield trend for phosphine oxide as compared to phosphonium signals, it was retained in **10**. A clear distinction of **9b** from its isomer **10b** (and from their *E*-isomers) was based on a ^{1}H NOESY NMR spectrum. It showed cross peaks for the *t*Bu and PMe signals as well as for the *t*Bu and olefinic CH signals, but not, however, for the PMe and olefinic CH signals.

EXPERIMENTAL

1,1,3,3,4-Pentaphenyl-1,3-diphospholium Bromide (**6a**)

A solution of 1.21 mL (9.7 mmol) of phenylbromoethyne in 50 mL of diethyl ether was added to the stirred solution of 3.74 g (9.7 mmol) of bis(diphenylphosphino)methane in 150 mL of ether. After 20 min the yellow product started to precipitate. It was collected on a closed frit after 4 days. Concentrating the filtrate gave a second crop. Yield: 4.23 g (77%) yellow powder; may be recrystallized from $CHCl_3$/ether, does not melt, turns black above 250°C. Anal. Calcd. for $C_{33}H_{27}BrP_2$ (565.4): C, 70.10; H, 4.81. Found: C, 69.78; H, 5.01.

Triphenyl(tert-*butylethynyl*)*phosphonium Tosylate*

A suspension of 1.0 g (2.2 mmol) of phenyl(*tert*-butylethynyl)iodonium tosylate [15] and 1.0 g (3.8 mmol) of triphenylphosphine was stirred overnight. Ether was added (5 mL) and the colorless product filtered off. Yield: 1.1 g (97%). The identity followed from the ^{1}H NMR spectrum showing the signals of *t*Bu, Me, and aryl protons with the proper intensities.

4-Tert-*butyl-1,1,3,3-tetraphenyl-1,3-diphospholium Tosylate* (**6b**)

Phenyl(*tert*-butylethynyl)iodonium tosylate (1.00 g, 2.2 mmol), when stirred at room temperature with a solution of 0.91 g (2.4 mmol) of bis(diphenylphosphino)methane in 25 mL of dry benzene, gradually dissolved. After 5 min a clear solution had formed from which overnight pale yellow crystal of **6b** precipitated. They were separated, washed with diethyl ether, and dried. Yield: 1.07 g (77%). Anal. Calcd. for $[C_{31}H_{31}P_2][C_7H_7O_3S]$ (636.7): C, 71.68; H, 6.02. Found: C, 70.99; H, 6.36.

(Z)-2-(*Diphenylphosphinoyl*)-1-*phenylethenyl-methyldiphenylphosphonium Bromide* (**9a**)

To 1.62 g (2.9 mmol) of **6a** in 15 mL of acetonitrile at room temperature was added 52 μL (2.9 mmol) of water. The yellow solution slowly turned colorless. After 24 h a $^{31}P\{^1H\}$ NMR spectrum showed the reaction to be complete yielding a 24:1 mixture of the isomers **9a** and **10a** (see Table 1). Evaporation of the solution in vacuo to half its volume and addition of 35 mL of ether gave a colorless precipitate of pure **9a**. Yield: 1.28 g (76%); mp 209–211°C. Anal. Calcd. for $C_{33}H_{29}BrOP_2$ (583.4): C, 67.94; H, 5.01. Found: C, 67.35; H, 5.27.

(Z)-1-tert-*Butyl-2-(diphenylphosphinoyl) ethenyl-methyldiphenyl-phosphonium Tosylate* (**9b**)

A sample of **6b** in dichloromethane solution, from which moist air was not excluded, changed over exclusively to **9b**. The reaction was monitored by ^{31}P NMR spectroscopy and was complete after a few days at room temperature. Evaporation of the solvent left colorless crystalline **9b**. ^{1}H NMR: δ(*t*Bu) = 1.3 (s, 9H); $\delta(TsO^-)$ = 2.3 (s, 3H), 7.1, 7.9 (AA'BB', N = 9.8 Hz, 2 + 2H). ^{13}C NMR: $\delta(TsO^-)$ = 21.2 (qt, $^1J_{CH}$ = 126.5, $^3J_{CH}$ = 4.4 Hz, Me), 144.5 (t, $^3J_{CH}$ = 7.8 Hz, C-1), 126.2 (dd, $^1J_{CH}$ = 162.5, $^3J_{CH}$ = 6.2, C-2), 128.2 (ddq, $^1J_{CH}$ = 157.3, $^3J_{CH}$ = 6.4, 5.0 Hz, C-3), 138.4 (tq, $^2J_{CH}$ = 6.4, $^3J_{CH}$ = 6.4 Hz, C-4). For other data see Tables 1 and 2.

ACKNOWLEDGMENT

We thank Dr. K. Karaghiosoff for his help with the NMR spectroscopic identifications. The work was supported by the Fonds der Chemischen Industrie and by the Cancer Institute of the NIH (2RO1 CA 16903).

REFERENCES

[1] For the modification of the cyclic bond system accompanying this exchange see: W. Schäfer, A. Schweig, K. Dimroth, H. Kanter, *J. Am. Chem. Soc., 98*, 1976, 4410.
[2] G. Märkl, *Angew. Chem., 75*, 1963, 669; *Angew. Chem. Int. Ed. Engl., 2*, 1963, 479.
[3] K. Dimroth, *Acc. Chem. Res., 15*, 1982, 58.
[4] G. Märkl, *Z. Naturforsch. B, 18*, 1963, 1136.

[5] E. Fluck, B. Neumüller, G. Heckmann, *Chem.-Ztg., 111*, 1987, 309; E. Fluck, G. Heckmann, W. Plass, P. G. Jones, *New J. Chem., 13*, 1989, 383; E. Fluck, W. Plass, G. Heckmann, H. Bögge, A. Müller, *Z. Naturforsch. B, 46*, 1991, 202.
[6] H. Schmidbaur, C. Paschalidis, O. Steigelmann, G. Müller, *Angew. Chem., 102*, 1990, 569; *Angew. Chem. Int. Ed. Engl., 29*, 1990, 516.
[7] M. A. Shaw, J. C. Tebby, R. S. Ward, D. H. Williams, *J. Chem. Soc. C*, 1970, 504.
[8] M. Davies, A. N. Hughes, S. W. S. Jafry, *Can. J. Chem., 50*, 1972, 3625.
[9] E. Fluck, G. Heckmann, W. Plass, M. Spahn, H. Borrmann, *J. Chem. Soc. Perkin Trans., 1*, 1990, 1223. $1\lambda^5,3\lambda^5$,5-Triphosphinines with one of the phosphorus ring members being two-coordinated (and thus corresponding in their electronic structure to the $1\lambda^5,3\lambda^5$-diphosphinines) have also recently been reported: E. Fluck, G. Becker, B. Neumüller, R. Knebl, G. Heckmann, H. Riffel, *Angew. Chem., 98*, 1986, 1018; *Angew. Chem. Int. Ed. Engl., 25*, 1986, 1002; E. Fluck, G. Becker, B. Neumüller, R. Knebl, G. Heckmann, H. Riffel, *Z. Naturforsch., B42*, 1987, 1213.
[10] Another example of this kind is given by the $1\lambda^5,4\lambda^5$-diphosphapentalen which has recently been reported: J. Silberzahn, H. Pritzkow, H. P. Latscha, *Angew. Chem., 102*, 1990, 815; *Angew. Chem. Int. Ed. Engl., 29*, 1990, 799; *Z. Naturforsch. B, 46*, 1991, 197.
[11] L. D. Quin: *The Heterocyclic Chemistry of Phosphorus*, Wiley, New York, 1981.
[12] F. Mathey, *Chem. Rev., 88*, 1988, 429.
[13] G. A. Bowmaker, R. Herr, H. Schmidbaur, *Chem. Ber., 116*, 1983, 3567.
[14] E. Fluck, B. Neumüller, G. Heckmann, H. Riffel, *Phosphorus Sulfur, 37*, 1988, 159.
[15] P. J. Stang, B. W. Surber, Zhen-Chu Chen, K. A. Roberts, A. G. Anderson, *J. Am. Chem. Soc., 109*, 1987, 228.
[16] C. E. Orzech, C. A. Welch, G. R. Ziegler, J. I. Dickstein, S. I. Miller, *J. Chem. Soc., 84*, 1962, 2020.
[17] H. G. Viehe, E. Franchimont, *Chem. Ber., 95*, 1962, 319.
[18] H. Hoffmann, H. Förster, *Tetrahedron Lett., 1964*, 983.
[19] J. I. Dickstein, S. I. Miller, *J. Org. Chem., 37*, 1972, 2168.
[20] G. A. Gray, *J. Am. Chem. Soc., 95*, 1973, 7736.
[21] M. A. Shaw, J. C. Tebby, R. S. Ward, D. H. Williams, *J. Chem. Soc. (C)*, 1970, 504.