

Exploration of isomeric bis(phosphanyl)-substituted carbenium ions: identification and synthesis of the most stable isomer †

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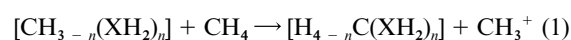
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Isomeric bis(phosphanyl) carbenium ions have been investigated by theoretical [MP2/6-31G(d,p) level of theory] and experimental means. On the potential energy surface (PES) of phosphorus cations of the formula $[P_2CH_3]^+$, five stable isomers are found. Their structures follow the stability order ($\Delta E_{rel}/kcal\ mol^{-1}$): P-protonated diphosphiranium, $[(H_2P)(HP)CH_2]^+$ **1a** (0.0) > C-phosphonio phosphalkene, $[H_3P-HC=PH]^+$ **2a** (4.5) \gg bis(phosphanyl) carbenium, $[CH(PH_2)_2]^+$ **3a** (18.5) > C-phosphanyl methylenephosphonium, $[H_2P-CH=PH_2]^+$ **4a** (22.6) \gg diphosphirenium, **5a** (47.1). The stability order is very different for the family of the four related stable $[P_2CH(NH_2)_4]^+$ ions **1b**, **2b**, **4b**, **5b** in which the phosphorus-bound hydrogens (and one carbon-bound hydrogen in the case of **1b**) have been replaced by NH_2 groups: **2b** (-39.6) \gg **1b** (0.0) > **5b** (2.2) \geq **4b** (3.7). None of these ions has a structure comparable to the classical amidinium ion $[HC(NH_2)_2]^+$. While all amino carbenium ions have a positively charged carbon atom, all phosphorus analogues carry a negative charge on carbon. In some, even the $p(\pi)$ -population exceeds unity suggesting that these should be considered as cationic methanides. Experimentally, a derivative of the diphosphiranium ion **1a** could be prepared by methylation of 1,2-bis-(2,4,6-tri-*tert*-butylphenyl)diphosphirane with MeO_3SCF_3 , and this new compound **8** was characterized by NMR methods. Although the most stable member in this family, it could only be observed under stable ion conditions ($T < -40\ ^\circ C$, five-fold excess of MeO_3SCF_3) and decomposes at higher temperatures.

1. Introduction

Investigations of phosphanyl-substituted carbenium ions have been motivated by the question of stabilizing formally the electron deficient centres by donor centres from the higher periods.^{1,2} Monophosphanyl-substituted carbenium ions, namely methylenephosphonium ions $[R_2C=PR_2]^+$, have been studied intensively.³⁻⁸ The bis(aminophosphanyl)-substituted ions $[HC\{P(NH_2)_2\}_2]^+$ have been calculated by Ahlrichs and coworkers at the MP2 level⁹ and very recently by Schoeller, Bertrand and coworkers using density functional theory (DFT) at the B3LYP/6-31G* level.^{10,11} In preliminary form, we have reported that various structures are found on the PES of $[P_2CH_3]^+$ cations of which actually none corresponds to the classical amidinium ion structure, *i.e.* an acyclic $[H_2P-CH-PH_2]^+$ structure with planar PH_2 groups. More recently, the tris(phosphanyl)-substituted cations $[C(PR_2)_3]^+$ ($R = H$,¹² NH_2 ¹³) being formally analogues of highly stabilized guanidinium ions, $[C(NR_2)_3]^+$,¹⁴ have been subjected to theoretical investigations. The results clearly show that phosphorus behaves as the better *intrinsic* π -donor when compared with nitrogen, *i.e.* $p(\pi)-P > p(\pi)-N$. Despite this, the stabilization exerted by these donor centres follows the inverse trend. The lower stability of the phosphorus cations is due to the energy that is necessary to force the phosphorus atom into a trigonal planar coordination sphere in order to make $p(\pi)$ -donation effective. While the methylene phosphonium ion $[H_2C=PH_2]^+$ is stabilized by about 65% of the iminium ion stabilization, the

methyl stabilization energy (MSE) ($kcal\ mol^{-1}$) calculated by the isodesmic reaction (1) for $[C(PH_2)_3]^+$ drops to about 55% of the guanidinium MSE,



where MSE for $n = 1$: $X = N$ 95; $X = P$ 62, and MSE for $n = 3$: $X = N$ 145.6; $X = P$ 80.6.

Hand in hand with this decrease goes an increasing pyramidalisation of the phosphorus centres, *i.e.* while the phosphorus atom is planar in $[H_2C=PH_2]^+$ and the P=C bond is short indicating a double bond, the phosphorus centres in $[C(PR_2)_3]^+$ ($R = H, NH_2$) are pyramidal and the C-P bonds are considerably longer.

The experimentally realised phosphanyl-substituted carbenium ions are shown in Fig. 1. Methylenephosphonium ions **I** with trigonal planar phosphorus centres are available with various substituents: $R = tBu, Ph, N^iPr_2$ and $R^1 = alkyl, aryl, silyl, GaCl_3$, *etc.*³⁻⁸ The P-planarisation energy is stored to some extent within these ions and that makes them highly

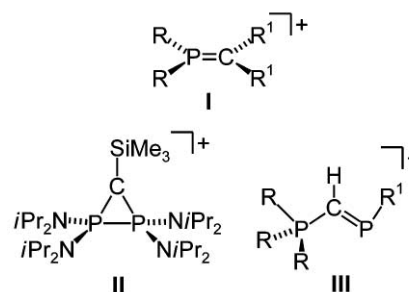
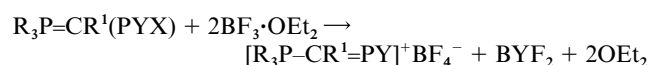


Fig. 1 Experimentally realised phosphanyl carbenium ions.

† Dedicated to Professor H.-F. Grützmaier on the occasion of his 70th birthday.

Electronic supplementary information (ESI) available: energy data for fragmentation reactions (a)-(c) and (a')-(c'). See <http://www.rsc.org/suppdata/dt/b2/b207749c/>

reactive and synthetically valuable building blocks in organo-phosphorus chemistry (the ‘phosphorus trick’¹⁵). Latest examples include the synthesis of heterocycles¹⁶ and the reductions of $[\text{RP}=\text{PR}_2]^+$ ¹⁷ or $[\text{R}_2\text{C}=\text{PR}_2]^+$ cations at low potentials leading to persistent phosphorus centred radicals.¹⁸ In elegant studies, Bertrand, Schoeller and coworkers have synthesized and completely characterized various derivatives of **II**, a cyclic valence isomer of a bis(phosphanyl)-substituted carbocation.^{10,11} Remarkably, this ion is an amino-substituted analogue of the least stable of all $[\text{P}_2\text{CH}_3]^+$ isomers. Phosphonio-substituted phosphalkenes **III** are well known^{19–22} and are most conveniently prepared from the reaction of phosphorus ylides, $\text{R}_3\text{P}=\text{CHR}^1$, and dihalophosphanes, X_2PR_2 ,²¹ or alkoxy- or aminophosphanyl-substituted phosphorus ylides and Lewis acids according to



where $\text{Y} = \text{OR}_2$, NR_2 .²⁰ Interestingly, the more ‘classical’ bis(phosphanyl)-substituted carbocations $[\text{HC}(\text{PR}_2)_2]^+$ are elusive. Karsch *et al.* suggested the formation of $[\text{HC}(\text{PPh}_2)_2]^+$ on the basis of a ³¹P NMR signal ($\delta = 67.3$) recorded when the P-chloro(phosphanylmethylene)phosphorane $[\text{ClPh}_2\text{P}=\text{CH}(\text{PPh}_2)]$ was reacted with AlCl_3 .²² Zavadskii *et al.* claim to have isolated the related cation, *i.e.* the C-phosphanyl methylene-phosphonium ion $[\text{Bu}_2\text{P}-\text{HC}=\text{P}(\text{N}^+\text{Pr}_2)\text{Me}]^+$ [$\delta(\text{PN}^+\text{Pr}_2)\text{Me} = 48.6$].²³ However, in view of the rather low frequency ³¹P resonances and the very recent results of Bertrand and coworkers,¹¹ who could trap these highly reactive ions but were unable to detect them spectroscopically, the identity of these species is doubtful. Here we wish to report our investigations concerning the synthesis and the properties of bis(phosphanyl)-substituted carbenium ions. The paper is divided into two parts: (i) a theoretical exploration of the PESs of bis(phosphanyl) carbenium ions $[\text{P}_2\text{CHR}_4]^+$ ($\text{R} = \text{H}, \text{NH}_2$); and (ii) a report on our experimental efforts which aimed at the synthesis of the most stable of all $[\text{P}_2\text{CH}_3]^+$ isomers, which turns out to be a yet unconsidered cyclic structure, namely a P-protonated diphosphirane. Our study emphasises the chemistry of alkyl- and aryl-substituted systems and supplements the previous investigations which concentrated on amino-substituted ions.^{9–11}

2. Results and discussion

Calculation of the $[\text{P}_2\text{CHR}_4]^+$ ($\text{R} = \text{H}, \text{NH}_2$) hyper surfaces

The PESs of the $[\text{P}_2\text{CH}_3]^+$ cations, **1a–5a** were explored at the MP2/6-31G(d,p) level of theory and the investigated structures are depicted in Fig. 2. For the purpose of comparison, we calculated also the tetra-amino derivatives $[\text{P}_2\text{CH}(\text{NH}_2)_4]^+$, **1b–5b**, shown in Fig. 3, which have been previously studied using DFT methods.^{10,11} The total energies (ΔE_{tot}), zero point energies (ZPE), relative energies (ΔE_{rel}), symmetry, and number of imaginary frequencies (N) of all species are given in Table 1. Selected bond lengths (Å) and angles (°) are given in Table 2.

$[\text{P}_2\text{CH}_3]^+$. We find five isomers as local minima on the $[\text{P}_2\text{CH}_3]^+$ PES. None of these has a structure that corresponds to the ‘classical’ amidinium ion structure. The closest analogue is species **3a** which has, however, significantly pyramidalised phosphorus centres. The P–C bonds in this C_2 symmetric isomer are shorter (*ca.* 7%) than usual P–C single bonds. They are, however, significantly longer (*ca.* 5.4%) than the P=C double bond in the methylenephosphonium ion, $[\text{R}_2\text{P}=\text{CR}^1_2]^+$. The next energetically higher isomer **4a** is just such a species, *i.e.* a C-phosphanyl-substituted methylenephosphonium ion. It is slightly less stable than **3a** (by 4.1 kcal mol⁻¹) and its structure can be obtained from **3a** by rotating one PH₂ group and flattening the other. The least stable isomer **5a** has a C_{2v} symmetric

Table 1 Energetics of **1a,b–5a,b**, **TS1–TS4**. Total energies, E_{tot} , are given in Hartrees, ZPEs and relative energies, ΔE_{rel} , are given in kcal mol⁻¹

		MP2/6-31(d,p)			
		E_{tot}	ZPE	N^a	ΔE_{rel}
1a	C_1	–722.299009	36.3	0	0.0
2a	C_s	–722.289719	34.9	0	4.5
3a	C_2	–722.264943	33.4	0	18.5
4a	C_s	–722.258311	33.3	0	22.6
5a	C_{2v}	–722.220911	34.4	0	47.1
TS1	C_1	–722.194287	31.5	1	61.0
TS2	C_1	–722.232058	33.5	1	39.3
TS3	C_1	–722.218620	31.6	1	45.8
TS4	C_1	–722.157750	32.2	1	84.6
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1b	C_1	–943.189272	82.2	0	0.0
2b	C_s	–943.251057	81.4	0	–39.6
3b	C_2	–943.170706	80.0	1	9.4
4b	C_1	–943.180139	80.2	0	3.7
5b	C_2	–943.184571	81.4	0	2.2

^a Number of imaginary frequencies.

structure with rather short P–C and P–P distances. This isomer is 28.6 kcal mol⁻¹ higher in energy than **3a** and its formation can be imagined by rotating both PH₂ groups in a position perpendicular to the PC₂ plane. Our results differ slightly from the DFT calculations¹¹ where the difference between **4a** and **5a** was found to be larger (34.6 kcal mol⁻¹) than in our calculations (24.5 kcal mol⁻¹). While **3a–5a** show the expected CH and PH connectivity for phospho-amidinium ions, the isomers **2a** and **1a** are obtained by H-migrations. Both isomers are considerably more stable than **3a** (**2a**: $\Delta E = 14$ kcal mol⁻¹; **1a**: $\Delta E = 18.5$ kcal mol⁻¹). The protonated diphosphirane **1a** is the global minimum on the $[\text{P}_2\text{CH}_3]^+$ PES.

In this work, we did not investigate the barriers for isomerisation which will convert the ions **3a**, **4a** and **5a**. These species are related by internal movements (*i.e.* rotations and flattening) of PH₂ groups and it is expected that these will be highly dependent on the actual substituents R used instead of H in experiments. For example, when bulky groups are employed the isomer **4a** should be preferred over isomer **3a**. Very large groups eventually may help to stabilize even the cyclic isomer **5a**. However, 1,2-shifts may cause an isomerisation of the high energy isomers to the more stable ones. We therefore inspected the reaction paths for the 1,2-H-shifts from **1a**→**2a** and from **1a**→**3a** and found that the transition states **TS1** and **TS2**, respectively, are rather high in energy. Hence, the ions **1a–3a** should be easily accessible by experiments if suitable precursors and synthetic methods can be found. The isomerisation of the least stable diphosphiranium **5a** into the more stable isomers **1a** or **2a** was also computed. The 1,2-H shift along the P²–P¹ vector which describes the transition **5a**→**2a** has a very small barrier (1.4 kcal mol⁻¹) when the ZPE correction is neglected. Inclusion of the ZPE correction reverses this energy order, *i.e.* the cyclic transition state **TS3** with a planar P¹–C–P²–H^{bridge} arrangement and a long P–P bond (2.677 Å) is slightly lower in energy than **5a**. On the other hand, the 1,2-H shift across the P²–C vector which transforms **5a** into the most stable cyclic isomer **1a** has a high barrier. The transition state **TS4** is 37.5 kcal mol⁻¹ higher in energy than **5a** and has a cyclic butterfly-type P¹–C–P²–H^{bridge} structure in which the P²–C bond is elongated to 2.325 Å.

$[\text{P}_2\text{CH}(\text{NH}_2)_4]^+$. As mentioned above, the P-amino-substituted cations of the general formula $[\text{P}_2\text{CH}(\text{NH}_2)_4]^+$ are not in the focus of our work but for comparison they were recalculated at the MP2/6-31G(d,p) level. Our results are shown in Fig. 3 and agree in most aspects with the ones (DFT) recently reported by Bertrand, Schoeller and coworkers.^{10,11} One differ-

Table 2 Selected bond lengths *a*, *b*, *c* (Å) and angles α , β , γ (°) of **1a,b–5a,b** and **TS1–TS4**. All values have been calculated at the MP2/6-31(d,p) level

	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	ΣP^1	ΣP^2
1a	1.800	1.893	2.165	71.7	56.1	51.1	355.7 ^a	236.9 ^a
1b	1.816	1.901	2.287	75.9	53.7	50.4	360.1 ^a	257.5 ^a
2a	1.782	1.691		121.0			—	
2b	1.747	1.685		118.5			—	
3a	1.724			130.6			322.1	
3b	1.712			133.8			337.6	
4a	1.870	1.645		120.4			281.6	
4b	1.855	1.625		119.4			291.1	
5a	1.697		2.104	76.6	51.7		345.9 ^a	
5b	1.708		2.094	75.6	52.2		353.2 ^a	
TS1	1.900	1.711	3.193	124.2				
TS2	1.876	1.745	3.245	127.3				
TS3^b	1.809	1.673	2.677	100.4	37.9	41.6		
TS4^c	1.691	2.324	2.217	64.8	71.6	43.6		

^a For the cyclic structures the sum of the basal X–P–P and X–P–X (X = H, NH₂) bond angles are given. ^b P¹–H^{bridge} 1.866 Å; P²–H^{bridge} 1.581 Å; P¹–H^{bridge}–P² 101.6°; P¹–H^{bridge}–P²C 1.3°. ^c C¹–H^{bridge} 2.186 Å; P²–H^{bridge} 1.398 Å; P¹–C–H^{bridge} 95.6°; C–H^{bridge}–P² 77.5°.

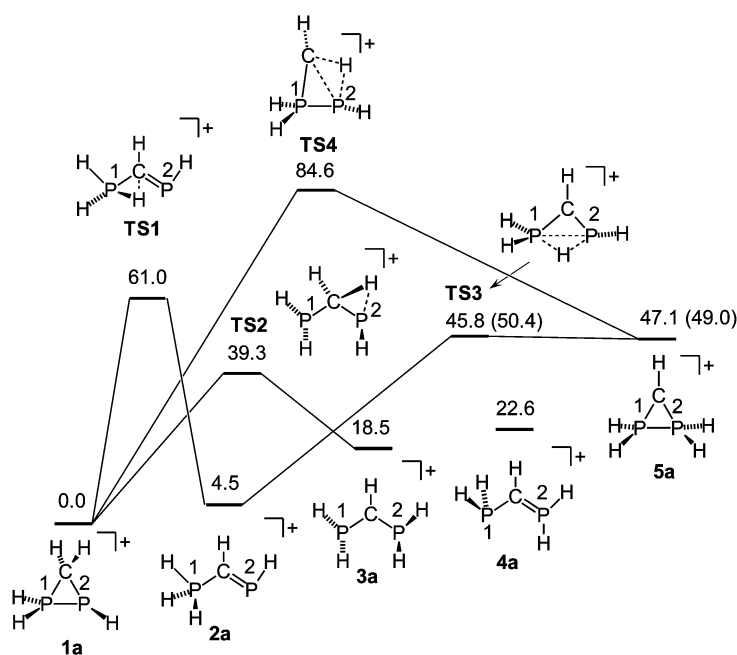


Fig. 2 Structures of **1a–5a** on the [P₂CH₃]⁺ PES. The 1,2-H-migrations *via* the transition states **TS1**, **TS2**, **TS3**, and **TS4** are shown. The value in parentheses for **TS3** corresponds to ΔE_{rel} without ZPE correction.

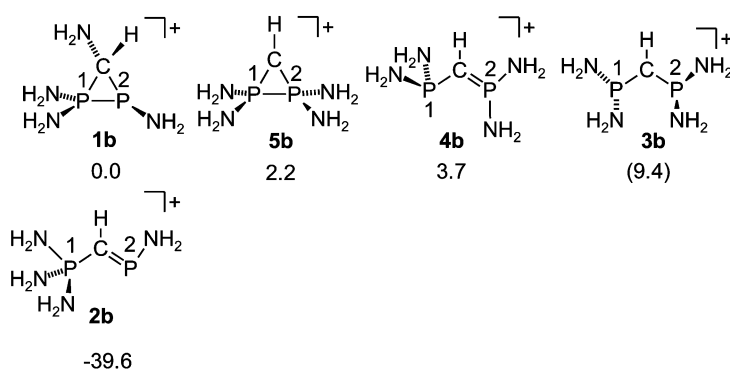


Fig. 3 Structures of **1b–5b** on the [P₂C(NH₂)₄H]⁺ PES. ΔE_{rel} is given under each formula. Structure **3b** is not a minimum but a transition state which rearranges towards **4b** upon geometry optimization.

ence is that we find **5b** to be slightly more stable than the acyclic ion **4b** at the MP2/6-31G(d,p) level (although only by 1.5 kcal mol⁻¹), whereas in the DFT calculations¹¹ the open form **4b**

was lower in energy (3.7 kcal mol⁻¹). Four stable isomers are located on the [P₂CH(NH₂)₄]⁺ PES and their stability order is different from **1a–5a**. The ion **3b** at the highest energy is not a

Table 3 Atomic and group NBO charges at the MP2/6-31(d,p) level of **1a,b-5a,b**

	P ¹		P ²		C	
	A ^a	G ^a	A	G	A	G
1a	0.67	0.86	0.54	0.54	-1.02	-0.40
1b	1.43	0.79	0.98	0.68	-0.68	-0.48
2a	0.91	1.09	0.67	0.66	-1.06	-0.75
2b	2.23	1.19	1.10	0.82	-1.30	-1.01
3a	0.66	0.77			-0.85	-0.54
3b	1.54	0.87			-1.05	-0.73
4a	0.42	0.45	0.90	1.08	-0.84	-0.53
4b	1.23	0.46	1.89	1.36	-1.12	-0.83
5a	0.85	0.92			-1.15	-0.83
5b	1.62	0.96			-1.21	-0.92

^a A: atom charge; G: group charge.

Table 4 σ - and π -Population at planar P² or C in **2a,b-5a,b** resulting from NBO analyses at the MP2/6-31(d,p) level

	P ²		C		N	
	p(σ)	p(π)	p(σ)	p(π)	p(σ)	p(π)
2a	3.53	0.72	3.80	1.21	—	—
2b	3.08	0.71	3.86	1.39	4.36	1.75
3a	—	—	3.85	0.96	—	—
3b	—	—	3.89	1.11	—	—
4a	2.96	1.05	3.84	0.94	—	—
4b	2.05	0.95	3.86	1.21	—	—
5a	—	—	3.58	1.51	—	—
5b	—	—	3.78	1.37	—	—

local minimum but a transition state and rearranges to cation **4b** which, as **4a**, can be described as a C-phosphanyl-substituted methylenephosphonium ion with one short P²=C and one longer P¹-C bond (see also ref. 13).

Interestingly, the model compound **5b** of the cyclic Bertrand ion **II** (see Fig. 1) is not an especially energy-rich species and groups well into the family **1b**, **5b**, and **4b**. Two isomers in the series of [P₂CH(NH₂)₄]⁺ ions are more stable than the symmetrical cyclic ion **5b**. The diphosphiranium ion **1b** is stabilized by 2.2 kcal mol⁻¹ with respect to **5b**. As the symmetrical cyclic diphosphiranium **5a** is remarkable due to its instability in the family of hydrogen-substituted ions, the P-amino-substituted phosphonio phosphalkene **2b** peaks out in the [P₂CH(NH₂)₄]⁺ family due to its high stability. This result is in agreement with experimental findings¹⁹⁻²² (see also ref. 33). We did not calculate the barriers for possible rearrangement reactions of the [P₂CH(NH₂)₄]⁺ ions. Experiments indicate that an amino group shift of the type **4b**→**2b** may occur rather easily when the transient [(Pr₂N)₂P=C(SiMe₃)(PPh₂)]⁺ cation is generated and the stable [(Pr₂N)P=C(SiMe₃)-PPh₂(NⁱPr₂)]⁺ ion is obtained in the reaction of [(Pr₂N)₂ClP=C(SiMe₃)(PPh₂)] with ECl₃ (E = Al, Ga).¹¹

Electronic properties. In order to obtain hints leading to a better understanding of the different stability orders and the electronic properties of the different isomers of the [P₂CHR₄]⁺ cations (R = H, NH₂), we calculated the atomic and group charges given by a Natural Bond Orbital (NBO) Analysis which are listed in Table 3. Furthermore, the σ - and π -populations of the phosphorus and carbon centres in molecules where these atoms reside in a planar coordination sphere were extracted from the NBO analysis. The results are compiled in Table 4.

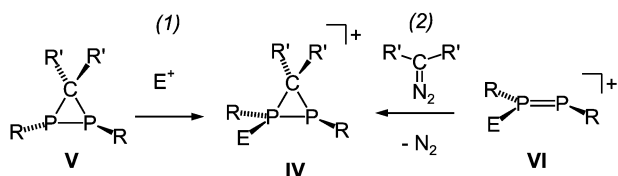
In all ions [P₂CHR₄]⁺, regardless of the substituents R, the carbon atom carries a negative charge whereas each phosphorus centre is positively charged, which is expected due to their electronegativities. It is also expected that in the NH₂-substituted systems the phosphorus atoms are higher positively

charged. The atomic charges A are most pronounced for the phosphonium centres (phosphorus with the formal oxidation state of +5). The P¹ centre in **2b** carries a particularly large positive charge (+2.23) which is the highest value among the cations. Note that the carbon atom of **2b** has also the largest negative charge. As a consequence, the P¹-C bond in **2b** (1.747 Å) is quite short due to Coulomb attraction. The particular high polarity and favourable charge alternation within the N ^{δ -}-P ^{δ +}-C ^{δ -}-P ^{δ +}-N ^{δ -} fragments in the amino-substituted ion **2b** might be the reason for the much higher stability of the isomer, which is particularly striking when it is compared with the parent system with R = H. Naturally, the differences between the H- and NH₂-substituted systems become smaller (and for P¹ in **1b** even reverse) when the group charges G are regarded. However, the general trend is maintained: The P-C bonds in the amino-substituted ions are significantly more polar. The cyclic systems **1b** and **5b** suffer from charge repulsion between the positively charged phosphorus atoms, which is, however, less important than the larger attraction between phosphorus and carbon and between phosphorus and nitrogen because the P-P bonds are much longer than the P-C and P-N bonds. In other words, the 'unusual' high stability of the symmetrical cyclic Bertrand ion is most probably due to high attractive Coulomb interactions.

An interesting question is in how far these ions may be still regarded as phosphanyl-substituted carbenium ions. It is well established that in many carbenium ions, [CR₃]⁺, the formally +1 (Lewis)-charged central tri-coordinated carbon centre bears a negative physical charge.²⁴ It was also demonstrated that strong σ -donation is as powerful in stabilizing electron deficient centres as π -donation.²⁵ These effects are also seen in the σ - and π -populations of the carbon centres of **2a,b-5a,b**. If we place the three valence electrons of the C⁺ atom into the σ -bonds, the excess of σ -electron density is simply given by p(σ) - 3 and ranges from 0.6 to 0.9 e. Noteworthy is the π -population at the carbon atom. In any carbenium ion apart from the parent methenium ion, [CH₃]⁺, the carbon π -orbital will be partially occupied either by π -donation from neighbouring lone pairs in an α -position or σ -bonds in a β -position (negative hyperconjugation^{24a,b}). However, in most of the [P₂CHR₄]⁺ ions, the π -population exceeds even unity. Interestingly, the p(π)-C occupation is especially high in the symmetrical cyclic structures **5a,b** where it comes close to or even exceeds the values in **2a,b** and **4a,b** although in these the carbon centres are involved in P=C double bonding. Thus, the formally electron deficient 3-coordinated carbon centers in the cyclic [P₂CHR₄]⁺ cations **5a,b** are actually electronically saturated which suggests that the term 'carbenium ion' is not really appropriate. Similar observations and conclusions have been made for chalcogeno-substituted carbenium ions, [C(XR)₃]⁺ especially for X = Te,²⁶ and the Bertrand ion **II**.^{10,11}

Synthesis of a diphosphiranium salt

Our calculations identified an unsymmetrical cyclic structure, namely the diphosphiranium salt **1a**, as the most stable isomer in the family of [P₂CH₃]⁺ ions. Of course, replacing the hydrogens by substituents R in experimental studies will strongly influence the energy scheme shown in Fig. 2. It may thus be possible that the phosphonio phosphalkene **2a** - the only structure for [P₂CHR₄]⁺ ions with R \neq NR₂ with known certainty - is actually more stable than **1a**. However, high barriers separate **1a** from the neighbouring forms **2a** and **3a** and even if the barriers will be also altered by R for H replacements, one can still expect that a derivative of **1a** is accessible by experiment. Hence, we became interested in the synthesis of a yet unknown diphosphiranium salt. For the preparation of such a diphosphiranium salt **IV** we envisioned the two general synthetic routes shown in Scheme 1: (i) reaction of a neutral diphosphirane **V** with a strong electrophile E⁺, or (ii) cyclo-



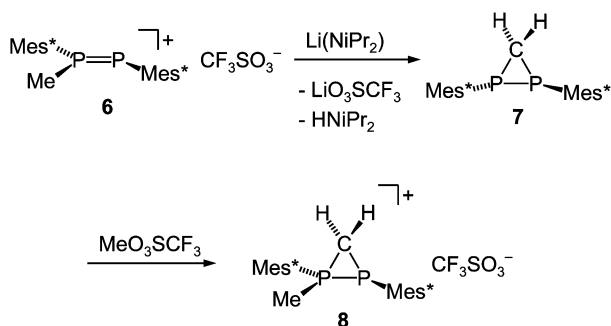
Scheme 1 General synthetic plan for the synthesis of a diphosphiranium salt.

addition of a diazomethane to the P=P double bond of a diphosphanylium ion **VI**.¹⁷

Although simple on paper, these reactions are quite challenging. The lone pairs of electrons on the phosphorus atoms in the three-membered rings have high *s*-orbital character²⁷ and thus make the phosphorus atoms reluctant to interact with electrophiles.²⁸

In our first experiments we used the *P,P*-bis(Mes*)-*C,C*-bis(phenyl)diphosphirane²⁹ [R = 2,4,6-*tert*-butylphenyl (Mes*) and R' = Ph in **V** of Scheme 1] which was treated with trifluoromethanesulfonic acid (HOTf). The ³¹P NMR spectrum of the reaction mixture showed only products resulting from P–P bond cleavage (singlets at $\delta = 10$ and 28). Also, addition of methyl triflate, MeO₃SCF₃, leads to ring cleavage, and by ³¹P NMR spectroscopy the phospho-alkene Mes*P=CPh₂³⁰ was unambiguously identified as the main product (40–50%) besides the diphosphanylium salt [Mes*MeP=PMe*]⁺CF₃SO₃[−] (**6**)¹⁷ (ca. 20%). A further singlet is observed at $\delta = 114.2$ which is compatible with the chemical shifts of P-functionalised phosphorus ylides^{5–7,16} and we propose the structure Mes*Me(CF₃SO₃)P=CPh₂ for this product. We then attempted the synthesis of a diphosphiranium salt **IV** by reacting **6** with trimethylsilyldiazomethane (TMSDM) [route (2) in Scheme 1]. The reaction is very slow and proceeds only when a large excess of TMSDM is used. Again the desired product was not observed and the phospho-alkenes *Z*- and *E*-Mes*P=CPh-(SiMe₃)³¹ were obtained as main products besides small quantities of several unidentified species.

In view of these results, we reasoned that any of the diphosphiranium salts eventually formed in these reactions may be sterically too congested and will decompose too rapidly preventing their direct observation. We therefore investigated the methylation of the sterically less hindered diphosphirane **7**. This compound has been previously reported but its isolation is quite laborious.³² We find that **7** can be easily prepared in pure form and with high yields by deprotonation of the diphosphanylium salt **6** with lithium di(isopropyl)amide (LDA) in acetonitrile as solvent (Scheme 2). Likely, the intermediate



Scheme 2 Synthesis of diphosphirane **7** and the diphosphiranium salt **8**.

Mes*P(=CH₂)(=PMe*) is formed in this reaction which undergoes an electrocyclic ring closure.³²

When a methylene chloride solution of **7** is reacted with one equivalent of MeO₃SCF₃, minor amounts of a new species are

detected. Addition of a five-fold excess of MeO₃SCF₃ drives the reaction to completion and the ³¹P NMR spectrum shows only two doublets, at $\delta = -95.4$ and -80.5 with a coupling constant of 261 Hz indicating a ¹J_{PP} coupling. Both signals are shifted to higher frequencies when compared with **7** ($\delta = -141$).³² Solutions of compound **8** are decomposed immediately upon contact with air and have only limited stability at room temperature. Attempts to crystallize **8** at low temperature failed because of its high solubility even in hydrocarbons. Furthermore, when the solutions are evaporated to dryness complete decomposition to a number of products was observed. Attempts to augment the readiness to form crystals by addition of B(O₃SCF₃)₃, whereby the diphosphiranium salt with [B(O₃SCF₃)₄][−] as the counter anion shall form, failed. Note, however, that no spectral changes were observed upon the addition of B(O₃SCF₃)₃ to a solution of **8** indicating the absence of notable cation anion contacts.

The diphosphiranium salt **8** was completely characterized by two-dimensional multinuclear NMR experiments in CD₂Cl₂ solution at a temperature below -40 °C which allowed the complete assignment of all ¹H and ¹³C signals in the remarkable complex spectra. In a P,H-correlated spectrum, strong cross signals are observed (i) between the methylated phosphorus nucleus P¹ and the methyl group, and (ii) between both phosphorus nuclei P¹ and P² and the diastereotopic methylene protons of the CH₂-bridge. These can be distinguished in that one signal, $\delta = 2.37$, shows a large coupling to P² of ca. 30–40 Hz. This proton points to the same side as the phosphorus lone pair. Furthermore, cross couplings from the phosphorus nuclei to the *meta*-aryl and the *tert*-butyl protons are observed. Using C,H long range correlations and a C,H-HMQC spectrum permitted the unambiguous assignment of the CH₂ carbon in the ¹³C NMR spectrum which shows a doublet of doublets at $\delta = 26.5$ with couplings of ¹J_{CP} = 31 Hz and ¹J_{CP} = 18 Hz. From the fine structure in the C,H cross peak these can be assigned to P¹ and P², respectively, having opposite signs. Because the rotation of the supermesityl residues, Mes*, is restricted at low temperature, all ¹H and ¹³C resonances for these groups appear separately, which explains the complex spectra.

3. Conclusions

Quantum chemical calculations demonstrate the diversity of stable structures on the PESs of bis(phosphanyl)-substituted carbenium ions. Remarkably, none of these correspond to the structure of the classical amidinium ion. In contrast to this especially stable α -amino-substituted carbenium ion, which carries a partial positive charge at the carbon centre, in most of the phosphorus analogues the carbon charges exceed even minus one. Partly this comes from substantial P→C σ -donation due to the elements' electronegativities, but in many of the phosphorus systems even the p(π)-population at the carbon centre exceeds unity. These cations are best described as cationic methanides.

The relative stability of the various [P₂CHR₄]⁺ isomers is highly dependent on the substituents and very different orderings are found for R = H or R = NH₂. As our calculations indicate, the directed synthesis of derivatives of most of the members of the [P₂CH₅]⁺ family **1a–5a** bearing alkyl or aryl groups instead of hydrogen shall be easily possible because the parent ions are already separated by sufficiently high activation barriers.³³ An exception may be an alkyl- or aryl-substituted derivative of the C_{2v} symmetrical cyclic ion **5a** which itself very easily isomerises. Note again that an analogous cyclic ion with N/Pr₂ groups could be isolated, emphasizing that amino- and alkyl/aryl-substituted systems are incongruous. The very high polarity and charge alternation within the amino-substituted ions [P₂CH(NH₂)₄]⁺ may be one reason for the different stabilities when compared with the less polar hydrogen system [P₂CH₅]⁺.

The most stable isomer from the family of $[P_2CH_5]^+$ ions is a P-protonated diphosphiranium ion consisting of a three-membered P_2C ring. According to calculations, this cyclic ion is stable as an isolated species in the gas phase and possible fragmentations are found to be quite endothermic.³⁵ However, attempts to prepare derivatives experimentally with R = alkyl and aryl indicate that such decomposition reactions occur in solution whereby the P–P bond is cleaved and phospho-alkenes are formed as main products. These fragmentations become more facile with high steric congestion of the ions. At the end, the synthesis of the diphosphiranium salt **8** was achieved by alkylation of the sterically less encumbered 1,2-bis(mesityl)diphosphirane **7** with a large excess of methyl triflate. Although **8** is persistent under stable ion conditions (*i.e.* low temperature and an excess of alkylating agent) it proved to be unstable in solution at ambient temperature. In particular, the observation that concentrating solutions of **8** led to decomposition indicates that, despite the absence of spectroscopic evidence, cation anion contacts may be responsible for this behaviour.

From the five stable isomers on the $[P_2CH_5]^+$ PES, derivatives of only two, *i.e.* **1a** and **2a**, have been observed experimentally to date. The isomers $[CH(EH_2)_2]^+$ with E = P, resembling most the classical amidinium ion with E = N, still await their synthesis, which we are currently investigating.

4. Experimental

Theoretical methods

All *ab initio* calculations were performed with the program package GAUSSIAN 94.³⁶ The hydrogen as well as NH_2 -substituted monocations of the formula $[P_2CH_5]^+$ (**1a–5a**) and $[P_2CH(NH_2)_4]^+$ (**1b–5b**), respectively, were calculated at the MP2/6-31G(d,p) level of theory including ZPE corrections. Vibrational frequencies were obtained to characterize their structures as minima or transition states.

For the various systems considered, atomic charges as well as orbital occupancies were calculated at the levels of optimization according to the NBO analysis developed by Weinhold and coworkers³⁷ and implemented in GAUSSIAN 94.

Syntheses

General techniques. All syntheses were performed in carefully dried glassware under an argon atmosphere which was passed through the Oxisorb[®]-gas purification system of Messer-Griesheim to remove the last traces of oxygen and moisture. All solvents were dried and purified using standard procedures and were freshly distilled under argon from sodium/benzophenone (THF), from sodium/diglyme/benzophenone (hexane) or calcium hydride (acetonitrile) prior to use. Air sensitive compounds were stored and weighed in a glove box (Braun MB 150 B-G system) and reactions on small scale were performed directly in the glove box. NMR spectra were either taken on the AMX-500, Avance DRX-400, Avance DPX-300, or Avance DPX-250 system. The chemical shifts are given as dimensionless δ values and were referenced against tetramethylsilane (TMS) for 1H and ^{13}C , 85% H_3PO_4 for ^{31}P , and $CFCl_3$ for ^{19}F NMR spectra. Coupling constants J are given in Hertz (Hz) and as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d or t for singlets, doublets and triplets, respectively. Broadened resonances are indicated as b.

^{13}C - 1H correlations were recorded with standard HMQC- and HMBC-methods. ^{31}P - 1H 2D spectra were recorded using the COSY method with 1H -detection, 1H - 1H TOCSY were taken with MLEV 17 mixing and for 1H - 1H NOESY experiments a mixing time of 600 ms was used. Mass spectra were taken on a Finnigan MAT SSQ 7000 in the EI (70 eV) mode. Melting points were determined in sealed capillaries using an apparatus fabricated by Büchi according to Dr Tottoli and are uncorrected.

Chemicals. Commercial chemicals were purchased from Fluka or Aldrich and used as delivered. The compounds $[Mes^*MeP=PMes^*]TfO$ (**6**)¹⁷ and 3,3-diphenyl-1,2-bis(Mes^{*})-diphosphirane²⁹ were prepared according to published procedures.

1,2-Bis[2,4,6-tri(*tert*-butyl)phenyl]diphosphirane (7)

$[Mes^*MeP=PMes^*]TfO$ (**6**) (312 mg, 0.44 mmol) and lithium diisopropylamide (70 mg, 0.65 mmol) were each dissolved in a small amount of acetonitrile and subsequently combined. The colour of the solution initially changed to green before the formation of a pale precipitate. The precipitate was filtrated from the solution and washed twice with small amounts of acetonitrile. The spectroscopically pure material can be recrystallized from a concentrated toluene solution which is layered with acetonitrile to give analytically pure diphosphirane **7** (215 mg, 0.38 mmol, 87%), mp 182 °C. Found: C, 78.4; H, 10.7. $C_{37}H_{60}P_2$ (566.82 g mol⁻¹) requires: C, 78.4; H, 10.7%. Selected NMR data: 1H NMR (CD_2Cl_2): δ 1.23 [s, 18 H, *p*-C(CH₃)₃], 1.61 (s, 2 H, CH₂), 1.72 [s, 36 H, *o*-C(CH₃)₃], 7.36 (s, 4 H, aryl-H); ^{13}C NMR (CD_2Cl_2): δ 30.5 (t, $J_{PC} = 24$ Hz, CH₂); ^{31}P NMR (C_6D_6): δ -141.0. MS: m/z (% ion): 566 (7, M⁺), 509 (74, M⁺ - 'Bu), 290 (34, Mes^{*}PCH₂⁺), 275 (60, Mes^{*}PCH₂⁺ - Me), 248 (100), 233 (46, M⁺ - 'Bu - Mes^{*}P), 57 (64, 'Bu⁺).

1-Methyl-1,2-bis[2,4,6-tri(*tert*-butyl)phenyl]diphosphiran-1-ium-trifluoromethane sulfonate (8)

The diphosphirane **7** (40 mg, 0.071 mmol) was dissolved in 0.5 mL CD_2Cl_2 in an NMR tube. The NMR tube was placed into a sufficiently long Schlenk flask which was cooled to -80 °C. Under a flow of argon, methyl triflate (57 mg, 38 μ l, 0.355 mmol) was added *via* a syringe and the NMR tube was closed. Attempts to isolate the product which formed in a very clean reaction were unsuccessful but **8** could be characterized by NMR spectroscopy at a temperature below -40 °C. 1H NMR (CD_2Cl_2 , -40 °C): δ 1.29 [s, 9 H, *p*-C(CH₃)₃], 1.30 [s, 9 H, *p*-C(CH₃)₃], 1.45 [s, 9 H, *o*-C(CH₃)₃], 1.46 (d, $^3J_{PH} = 1$ Hz, 3 H, P-CH₃), 1.49 [s, 9 H, *o*-C(CH₃)₃], 1.61 [s, 9 H, *o*-C(CH₃)₃], 1.67 [s, 9 H, *o*-C(CH₃)₃], 2.37 (b, 1 H, P-CH₂-P), 2.40 (1 H, P-CH₂-P), 7.36 (s, 1 H, aryl-H), 7.47 (s, 1 H, aryl-H), 7.49 (s, 1 H, aryl-H), 7.61 (s, 1 H, aryl-H). ^{13}C NMR (CD_2Cl_2 , -40 °C): δ 12.9 (d, $J_{PC} = 32.4$ Hz, P-CH₃), 26.5 (dd, $J_{CP} = 31$ Hz, $J_{CP} = 18$ Hz, P-CH₂-P), 30.5 [s, *p*-C(CH₃)₃], 30.5 [s, *p*-C(CH₃)₃], 33.2 [s, *o*-C(CH₃)₃], 33.5 [d, $J_{PC} = 3.2$ Hz, *o*-C(CH₃)₃], 33.9 [s, *o*-C(CH₃)₃], 34.3 [s, *o*-C(CH₃)₃], 34.9 [s, *o*-C(CH₃)₃], 35.3 [s, *o*-C(CH₃)₃], 39.5 [s, *o*-C(CH₃)₃], 40.1 [s, *o*-C(CH₃)₃], 40.6 [s, *p*-C(CH₃)₃], 40.8 [s, *p*-C(CH₃)₃], 110.0 (d, $J_{PC} = 68.3$ Hz, *i*-C), 120.5 (s, *i*-C), 123.7 (s, *m*-C), 125.1 (d, $J_{PC} = 15.1$ Hz, *m*-C), 127.1 (s, *m*-C), 128.7 (d, $J_{PC} = 12.6$ Hz, *m*-C), 152.9 (d, $J_{PC} = 2.5$ Hz, *p*-C), 156.6 (d, $J_{PC} = 3.4$ Hz, *p*-C), 160.3 (s, *o*-C), 160.7 (s, *o*-C), 160.8 (s, *o*-C), 161.7 (s, *o*-C). ^{31}P NMR (CD_2Cl_2 , -40 °C): δ -95.4 (d, Mes^{*}P), -80.5 (d, Mes^{*}MeP), $J_{PP} = 260.7$ Hz.

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