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Bis(methylene)- $\lambda^5$ -phosphane anions†Akihiro Nomoto,<sup>a</sup> Koh Sugamata<sup>id</sup>\*<sup>b</sup> and Takahiro Sasamori<sup>id</sup>\*<sup>acc</sup>

Bis(methylene)- $\lambda^5$ -phosphane anions, *i.e.*, anionic phosphorus-centered heteroallene-type molecules, were obtained from the desilylation of a bis(silyl)methyl-substituted phosphalkene. Their molecular structures, which were determined using spectroscopic techniques and single-crystal X-ray diffraction analysis, suggest that the central di-coordinated P atom is engaged in cumulative C=P=C  $\pi$ -bonds with the neighboring C atoms. The  $\pi$ -bond character of the C=P=C moieties was examined on the basis of the experimental results in combination with theoretical calculations; the results obtained suggest that multiple silyl substitutions at the C atom weaken the C=P  $\pi$ -bonding character.

## Introduction

Bis(methylene)- $\lambda^5$ -phosphanes, *i.e.*, phosphorus-centered heteroallene-type molecules, have attracted much attention as valence isomers of  $\sigma^3, \lambda^5$ -phosphiranes owing to their expected unique bonding character due to the cumulative C=P  $\pi$ -bonds. In 1982,<sup>1</sup> Appel reported the first example of isolable bis(methylene)- $\lambda^5$ -phosphanes (**I<sup>R</sup>**, R = C<sub>6</sub>H<sub>11</sub>, Ph, and Me<sub>2</sub>N), whose structural characterization revealed a cumulative C=P=C  $\pi$ -bond with a tri-coordinated P(v) atom. This  $\sigma^3, \lambda^5$ -phosphane, *i.e.*, a phosphorus(v)-centered allene, represented a milestone in main-group-element chemistry as an unprecedented low-coordinated organophosphorus compound alongside West's disilene and Yoshifuji's diphosphene.<sup>2,3</sup> The hitherto isolated bis(methylene)- $\lambda^5$ -phosphanes exhibit a distinct bent-allenic structure that is significantly different from the linear structure of all-carbon allenes.<sup>4</sup> Bis(methylene)- $\lambda^5$ -phosphanes have so far been obtained by treating the corresponding carbenes or carbenoids with the corresponding phosphalkenes.<sup>5</sup> Furthermore, the *P*-chloro-substituted analogues of bis(methylene)- $\lambda^5$ -phosphanes (**I<sup>Cl</sup>**, Fig. 1) can be expected to serve as suitable precursors to a variety of functionalized bis(methylene)- $\lambda^5$ -phosphanes, given that **I<sup>Cl</sup>** can be easily functionalized at the phosphorus atom *via* nucleophilic substitution reactions (Fig. 1a).<sup>6–11</sup> The diverse reactivity of bis(methylene)- $\lambda^5$ -phosphanes prompted us to focus our attention on the synthesis of a *P*-anionic bis(methylene)- $\lambda^5$ -phosphane, which is expected to work as a nucleophilic building

block for hitherto unknown types of bis(methylene)- $\lambda^5$ -phosphanes.

Recently, we have successfully synthesized stable bis(methylene)- $\lambda^4$ -sulfane (**II**, Fig. 1), which represents the first example of a group-16-element-centered heteroallene, using steric stabilization afforded by silyl groups.<sup>12</sup> Moreover, its heavier-element analogues, *i.e.*, bis(methylene)- $\lambda^4$ -selane **III** and -tellane **IV**, have been synthesized and fully characterized.<sup>13,14</sup> These bis(methylene)- $\lambda^4$ -chalcogenanes, which exhibit pseudo-*C*<sub>2v</sub> symmetric coordination geometries with bent allene-type electronic structures, can be interpreted as “2-heteroallenes”,<sup>15</sup> characterized by the three-center-four-electron  $\pi$ -bond on the C=Ch=C (Ch = S, Se, Te) moiety. Given that bis(methylene)- $\lambda^4$ -chalcogenanes are isolobal to anionic group-15-

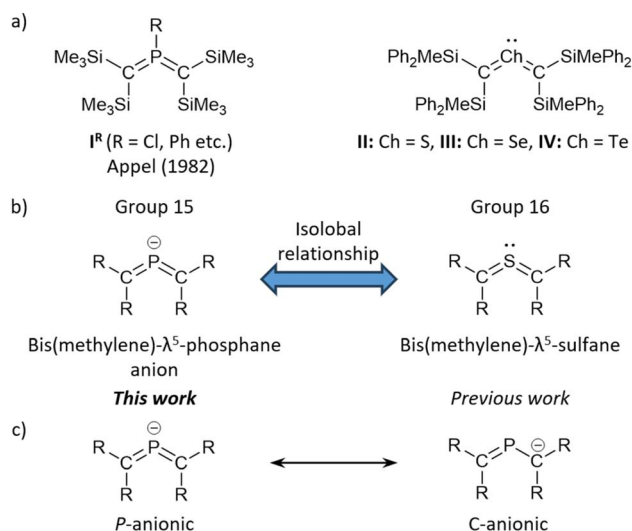


Fig. 1 (a) Isolated bis(methylene)- $\lambda^5$ -phosphanes **I<sup>R</sup>** and bis(methylene)- $\lambda^4$ -chalcogenanes **II–IV**. (b) Isolobal relationship between bis(methylene)- $\lambda^5$ -phosphane anion and bis(methylene)- $\lambda^4$ -sulfane. (c) Canonical resonance structures of bis(methylene)- $\lambda^5$ -phosphane anions.

<sup>a</sup>Graduate School of Science and Technology, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan. E-mail: sasamori@chem.tsukuba.ac.jp

<sup>b</sup>Department of Chemistry, College of Science, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan. E-mail: sugamata@rikkyo.ac.jp

<sup>c</sup>Division of Chemistry, Institute of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan

<sup>d</sup>Tsukuba Research Center for Energy Materials Sciences (TREMS), University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan

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element-centered 2-heteroallenes (Fig. 1b), we expected that anionic bis(methylene)- $\lambda^5$ -phosphanes could potentially be synthesized using sterically demanding silyl groups as in the cases of **II–IV**, which may prevent the isomerization to the corresponding phosphiranides.<sup>16,17</sup> As described above, bis(methylene)- $\lambda^5$ -phosphane anions should be of great interest not only with respect to their expected unique electronic properties, but also with regard to their potential as precursors to further functionalized bis(methylene)- $\lambda^5$ -phosphanes upon treatment with electrophiles or electron-deficient metals. Moreover, a detailed examination of the intrinsic nature of these species, *i.e.*, whether they should be considered *P*-anionic bis(methylene)- $\lambda^5$ -phosphanes or *C*-anionic phosphoalkenes, would be of great importance and interest (Fig. 1c). Here, we present the successful isolation of bis(methylene)- $\lambda^5$ -phosphane anions and their structural characterization.

## Results and discussion

To start with, we attempted the synthesis of *P*-chlorophosphaallene **A** as a precursor for the bis(methylene)- $\lambda^5$ -phosphane anions according to a previously reported protocol.<sup>18</sup> The reaction of bis(silyl)carbenoid  $R^{Si}_2CBrLi$  ( $R^{Si} = SiMePh_2$ ) with 0.33 equivalents of  $PCl_3$  was carried out. Specifically, the treatment of a THF/ $Et_2O$  solution of the bis(silyl)carbenoid, which was prepared *via* the lithiation of  $R^{Si}_2CBr_2$  using *t*-BuLi at  $-110$  °C, with 0.33 equivalents of  $PCl_3$  in  $Et_2O$  afforded phosphoalkene **1** in 31% yield without the formation of the expected product (**A**) (Scheme 1). Compound **1**, which is air- and moisture-stable, was purified by column chromatography on  $SiO_2$  using  $CH_2Cl_2$ /hexane as the eluent. The molecular structure of **1** was characterized by spectroscopic techniques and single-crystal X-ray diffraction (SCXRD) analysis (Fig. 2).<sup>19</sup> The  $^{31}P$  NMR chemical shift of **1** (436.5 ppm) is close to those of related phosphoalkenes (*ca.* 378–439 ppm).<sup>20–22</sup> The theoretically estimated value of the chemical shift of **1** ( $\delta_P = 470$  ppm) based on gauge-independent atomic orbital (GIAO) NMR calculations is consistent with the experimental results,<sup>23</sup> suggesting  $\pi$ -bond character for the  $C=P$  bond in solution and a negligible solvent effect. The  $P1-C1$  bond length of **1** (1.675(2) Å) is almost identical to those of the related phosphoalkenes (*ca.* 1.66 Å)<sup>20,21,24</sup> and considerably shorter than the  $P1-C2$  bond of **1** (1.835(2) Å), suggesting a double- and single-bond character for the  $P1=C1$  and  $P1-C2$  bonds, respectively. In contrast to the tetrahedral geometry of the  $C2$  atom, the  $C1$  atom features a trigonal planar geometry with a bond-angle sum of  $360^\circ$  around the  $C1$  atom. To elucidate the reaction mechanism, we examined the trapping reactions of the lithiated species generated *in situ* by the addition of  $CH_3I$  in the reaction of  $R^{Si}_2CBr_2$  with *t*-BuLi.<sup>25</sup> The treatment of  $R^{Si}_2CBr_2$  with 2.9 eq. of

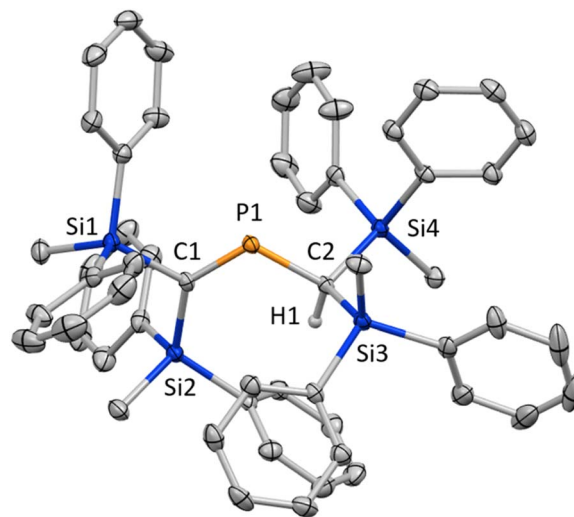
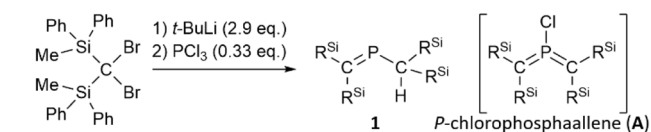


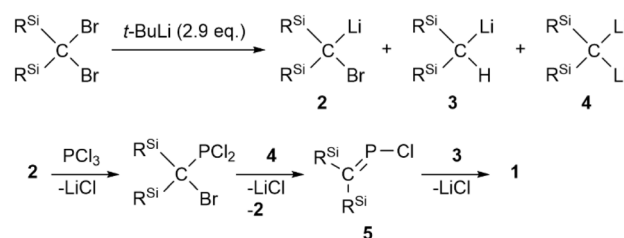
Fig. 2 Molecular structure of **1** in the crystalline state with thermal ellipsoids at 50% probability; all hydrogen atoms except for H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]:  $C1-P1$  1.675(2),  $P1-C2$  1.835(2), and  $C1-P1-C2$  112.63(9).<sup>19</sup>

*t*-BuLi followed by the addition of an excess amount of  $CH_3I$  resulted in the formation of three methylated compounds derived from the intermediates of bis(silyl)carbenoid **2**, lithium bis(silyl)methanide **3**, and dilithio compound **4** (Scheme S1†). The mechanism for the formation of **1** remains unclear at this stage, even though it seems feasible to assume that **1** is formed *via* the generation of *P*-chlorophosphaalkene **5** as a reactive intermediate, followed by its reaction with lithium bis(silyl)methanide **3** together with the elimination of  $LiCl$  (Scheme 2).

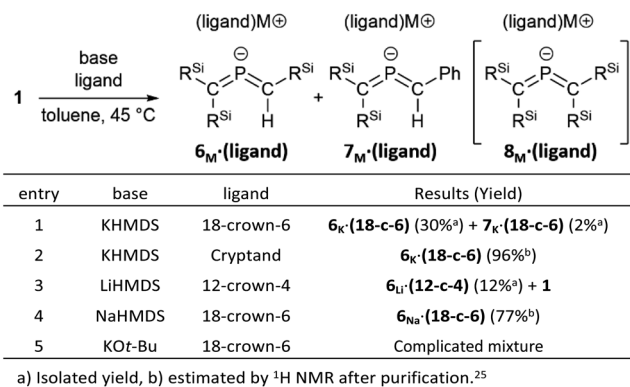
Subsequently, we attempted the deprotonation of **1** in the expectation of the formation of bis(methylene)- $\lambda^5$ -phosphane anion **8<sub>K</sub>** (**18-c-6**) *via* an E2-elimination using potassium hexamethyldisilazide (KHMDs) in the presence of 18-crown-6 in toluene. However, unexpectedly, desilylated compounds **6<sub>K</sub>** (**18-c-6**) (30%) and **7<sub>K</sub>** (**18-c-6**) (2%) were obtained as crystalline compounds (Scheme 3; entry 1). In the case of using a cryptand instead of 18-crown-6, only **6<sub>K</sub>** (**cryptand**) was formed (entry 2). Using  $LiHMDS$  or  $NaHMDS$  as a base also furnished **6<sub>M</sub>** (**ligand**) exclusively (entries 3 and 4). In contrast, when  $KOt$ -Bu in combination with 18-crown-6 was used instead of KHMDs/18-crown-6, a complicated mixture was obtained.



Scheme 1 The synthesis of phosphoalkene **1**.



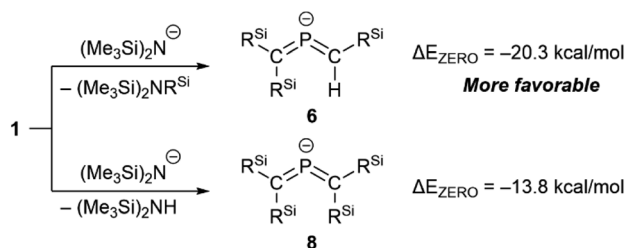
Scheme 2 Plausible reaction mechanism for the formation of phosphoalkene **1**.



Scheme 3 The synthesis of bis(methylene)- $\lambda^5$ -phosphane anions **6<sub>M</sub>(ligand)** and **7<sub>M</sub>(ligand)**.

Accordingly, it can be concluded that it is crucial to use the HMDS anion for the generation of **6<sub>M</sub>(ligand)**, and that the accompanied potassium cation causes the simultaneous formation of **7<sub>K</sub>(ligand)**. The formation of **6<sub>M</sub>(ligand)** should most likely be interpreted in terms of a favorable nucleophilic attack of the HMDS anion on the electrophilic Si atom, even though the details of the mechanism for the formation of **7<sub>K</sub>(ligand)** remain unclear at this stage.<sup>26</sup> As shown in Scheme 4, theoretical calculations suggested that the formation of **6** together with amino silane (Me<sub>3</sub>Si)<sub>2</sub>NSiMePh<sub>2</sub> in the reaction of **1** with the HMDS anion should be thermodynamically more favorable ( $\Delta E_{\text{ZERO}} = -20.3 \text{ kcal mol}^{-1}$ ) compared to the reaction of phosphalkene **1** with (Me<sub>3</sub>Si)<sub>2</sub>N<sup>-</sup> to give tetrasilyl bis(methylene)- $\lambda^5$ -phosphane anion **8** and (Me<sub>3</sub>Si)<sub>2</sub>NH ( $\Delta E_{\text{ZERO}} = -13.8 \text{ kcal mol}^{-1}$ ). To further investigate the reaction mechanism for the desilylation reaction, we performed theoretical calculations on the potential energy surface of both a deprotonation reaction and a desilylation reaction of the phosphalkene (**SM**) using model compounds as shown in Fig. S55.† The reaction barrier for the deprotonation product *via* **TS1** is smaller than that of the desilylation product *via* **TS2**, while the product of the desilylation reaction (**Pr2**) is significantly stable compared to that of the deprotonation reaction (**Pr1**). As a result, it was found that the formation of bis(methylene)- $\lambda^5$ -phosphane anion **6** is a thermodynamically favored reaction.

Bis(methylene)- $\lambda^5$ -phosphane anions **6<sub>K</sub>(18-c-6)** and **7<sub>K</sub>(18-c-6)** exhibit moderate thermal stability in the solid state (**6<sub>K</sub>**, m.p.: 93 °C (decomp); **7<sub>K</sub>**, m.p.: 53 °C (decomp.)) and high

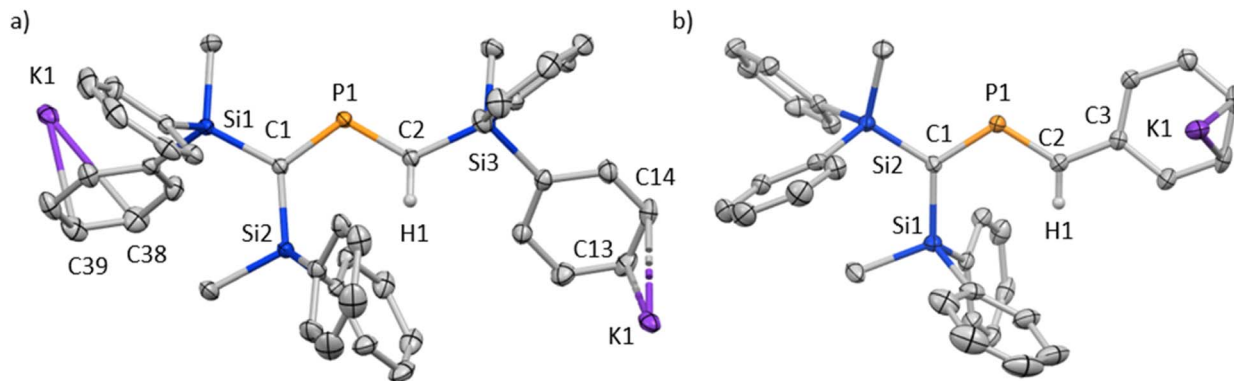


Scheme 4 Comparison of  $\Delta E_{\text{ZERO}}$  between the desilylation and deprotonation reactions of **1**.

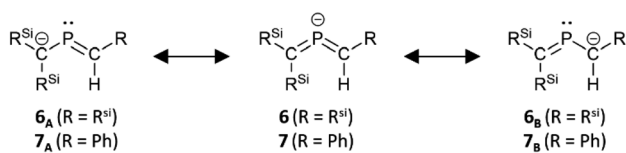
thermal stability in solution, *i.e.*, the NMR spectra of **6<sub>K</sub>(18-c-6)** and **7<sub>K</sub>(18-c-6)** in C<sub>6</sub>D<sub>6</sub> remained unchanged after 24 h at 80 °C.

The characterization of **6<sub>K</sub>(18-c-6)** and **7<sub>K</sub>(18-c-6)** was accomplished by multinuclear NMR and UV-vis spectroscopy, mass spectrometry, and SCXRD analysis.<sup>19</sup> In the molecular structures of **6<sub>K</sub>(18-c-6)** and **7<sub>K</sub>(18-c-6)** (Fig. 3), both the protons on C2 of **6<sub>K</sub>(18-c-6)** and **7<sub>K</sub>(18-c-6)** were located based on the residual Q-peaks, which represent residual electron density peaks in the differential electron-density map, in the LSQ process (see the ESI†). In the crystal structure of **6<sub>K</sub>(18-c-6)**, the potassium cation is coordinated by an 18-crown-6 ether and two phenyl rings, which results in the formation of an infinite chain structure in the solid state (Fig. 3a and S42†). In contrast, in **7<sub>K</sub>(18-c-6)**, the potassium cation is coordinated by an 18-crown-6 ether and one phenyl ring connected to the allene moiety, resulting in a monomeric structure. It should also be noted here that the phenyl ring is co-planar to the C=P=C moiety, probably due to  $\pi$ -conjugation, which is indicative of the considerable  $\pi$ -bond character of both C=P bonds. The central C=P=C moiety in **6<sub>K</sub>(18-c-6)** is bent (C1–P1–C2: 112.23(5)°) with almost identical C=P bond lengths (C1–P1: 1.723(1) Å; P1–C2: 1.694(1) Å). In the case of **7<sub>K</sub>(18-c-6)**, the allene moiety also shows a bent allene-type structure (C1–P1–C2: 112.6(1)°; C1–P1: 1.717(2) Å; P1–C2: 1.690(3) Å). The C–P bonds are considerably shorter than typical C–P single bonds (*e.g.*, 1.835(2) Å in **1**) but slightly longer than typical C=P double bonds (*e.g.*, 1.675(2) Å in **1**). The fact that the C1 = P1 bond (1.723(1) Å) is slightly longer than the C2 = P1 bond (1.694(1) Å) should most likely be rationalized in terms of the predominant contribution of the resonance structure of bis(methylene)- $\lambda^5$ -phosphane anion **6** bearing the C=P=C allenic  $\pi$ -bonds along with the partial contributions of 2-phosphapropenyl anion **6<sub>A</sub>** rather than **6<sub>B</sub>** (Fig. 4), wherein the anion charge is partially localized on the C1 atom probably due to the considerable  $\sigma$ -effect of the two adjacent silyl groups. The C1–P1 bonds (1.716(3) Å and 1.717(2) Å) in **7<sub>K</sub>(18-c-6)** are slightly longer than the P1–C2 bonds (1.694(3) Å and 1.690(3) Å) and those of **6<sub>K</sub>(18-c-6)**. These structural features are similar to those of a previously reported bis(methylene)- $\lambda^4$ -sulfane.<sup>12</sup> In contrast, as shown in Fig. 5, the dihedral angles ( $\varphi$ ) between the two terminal carbon planes of the allene moieties in **6<sub>K</sub>(18-c-6)** (8.4°) and **7<sub>K</sub>(18-c-6)** (4.5°/3.4°) are very small, suggesting an almost coplanar geometry, which is different from that of the reported bis(methylene)- $\lambda^4$ -sulfane (51.9°). Theoretical calculations indicated that the dihedral angles between the terminal carbon planes of the allene moieties ( $\varphi$ ) tend to increase with increasing steric demand of the substituents on the terminal carbons (Fig. S46†). Thus, it can be concluded that a bis(methylene)- $\lambda^5$ -phosphane anion should exhibit an intrinsically coplanar geometry. Moreover, the C1–P1–C2 bond angles of **6<sub>K</sub>(18-c-6)** (112.23(5)°) and **7<sub>K</sub>(18-c-6)** (112.6(1)°) are almost the same as that of **1** (112.6(1)°), but significantly narrower than those of the hitherto reported bis(methylene)- $\lambda^5$ -phosphanes (127–137°),<sup>7</sup> indicating high s-character for the lone pair on the phosphorus atoms of **6<sub>K</sub>(18-c-6)** and **7<sub>K</sub>(18-c-6)** as well as high p-character of R–P(=C)<sub>2</sub>  $\sigma$ -/ $\pi$ -bonds.

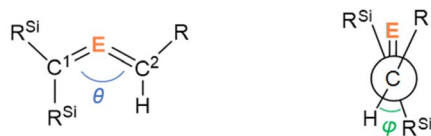




**Fig. 3** (a) Molecular structure of  $6_K$  (**18-c-6**) in the crystalline state with thermal ellipsoids at 50% probability; all hydrogen atoms except for H1 and 18-crown-6 are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.723(1), P1–C2 1.694(1), and C1–P1–C2 112.23(5). (b) Two independent molecules ( $7_K$ -A and  $7_K$ -B) were found in the unit cell. Molecular structure of one of the two crystallographically independent molecules in the unit cell of  $7_K$  (**18-c-6**) in the crystalline state with thermal ellipsoids at 50% probability; all hydrogen atoms except for H1 and 18-crown-6 are omitted for clarity. Selected bond lengths [Å] and angles [°] [ $7_K$ -A]: C1–P1 1.717(2), P1–C2 1.690(3), C2–C3 1.449(3), C1–P1–C2 112.6(1) [ $7_K$ -B]: P2–C47 1.716(3), C48–P2 1.694(3), and C48–P2–C47 112.5(1).<sup>19</sup>



**Fig. 4** Canonical resonance structures of bis(methylene)- $\lambda^5$ -phosphane anions **6** and **7**.



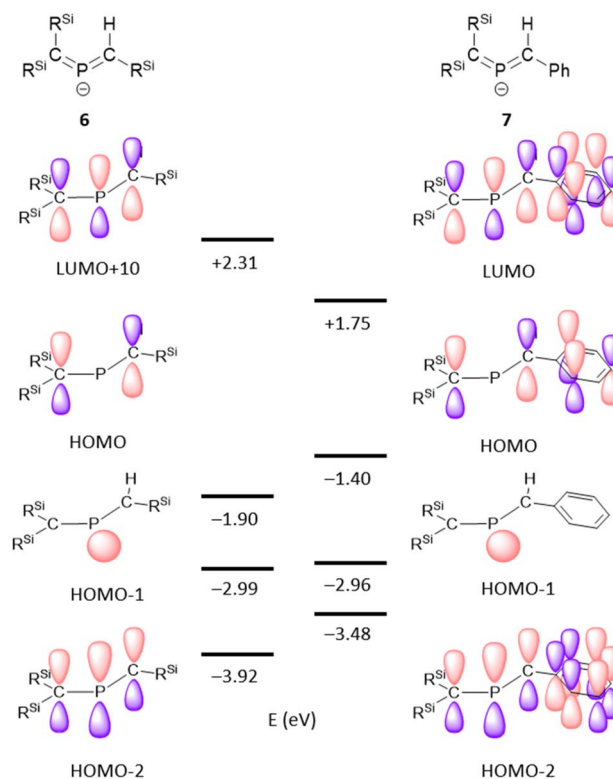
	E = P <sup>-</sup> , R = R <sup>Si</sup>	E = S, R = Ph	E = P <sup>-</sup> , R = Ph	E = S, R = Ph
C1=E (Å)	1.723(1) <sup>a</sup>	1.648 <sup>b</sup>	1.717(2) <sup>a</sup>	1.654 <sup>b</sup>
E=C2 (Å)	1.694(1) <sup>a</sup>	1.632 <sup>b</sup>	1.690(3) <sup>a</sup>	1.640 <sup>b</sup>
$\theta$ (°)	112.23(5) <sup>a</sup>	115.99 <sup>b</sup>	112.6(1) <sup>a</sup>	114.03 <sup>b</sup>
$\varphi$ (°)	8.42 <sup>a</sup>	4.27 <sup>b</sup>	4.47 <sup>a</sup>	8.54 <sup>b</sup>
NPA	-1.7, +0.8, -1.4	-1.4, +0.8, -1.0	-1.7, +0.7, -0.7	-1.4, +0.7, -0.5
(C1, E, C2)				

a) Experimental values, b) calculated values.

**Fig. 5** Comparison of structural parameters between bis(methylene)- $\lambda^5$ -phosphane anions and bis(methylene)- $\lambda^4$ -sulfanes.

The structural optimization of bis(methylene)- $\lambda^5$ -phosphane anions **6** and **7** using DFT calculations<sup>23</sup> was able to closely reproduce the experimentally observed structures (Fig. S43 and S44†). Natural-bond-orbital (NBO) calculations on the optimized structure of **6** showed one lone pair at the P atom (HOMO–1), two C–P  $\sigma$ -bonds, and a 3-center-4-electron  $\pi$ -bond on the C–P–C moiety as the LUMO+10 (anti-bonding), HOMO ( $\pi^*(\text{P}=\text{C})$ ), and HOMO–2 ( $\pi(\text{P}=\text{C})$ ) (Fig. 6).<sup>23</sup> On the other hand, the 3-center-4-electron  $\pi$ -bond in **7** is composed of the LUMO (anti-bonding), HOMO (non-bonding), and HOMO–2

(bonding), whereby the HOMO–LUMO gap is narrowed by the  $\pi$ -conjugation with the attached phenyl group. The estimated bond orders of the C–P bonds in **6** and **7**, based on their Wiberg bond indices (WBIs) of 1.48 (P1–C2) and 1.24 (C1–P1) for **6**, as well as 1.45 (P1–C2) and 1.24 (C1–P1) for **7**, are slightly smaller than that of the C=P double bond in **1** (1.66) and larger than the value for the C–P single bond in **1** (0.91), indicating  $\pi$ -bonding character for the C–P bonds in **6** and **7**. The calculated natural population analysis (NPA) charge on the phosphorus



**Fig. 6** Kohn–Sham orbitals of **6** (left) and **7** (right), calculated at the B3PW91-D3(bj)/6-311G(3d) level.

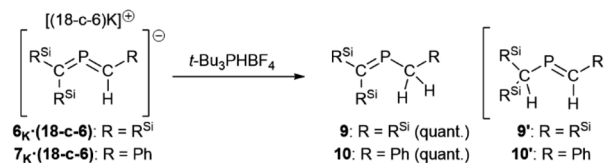


atom was +0.8 for **6** and +0.7 for **7**, while the charges on the adjacent carbon atoms were  $-1.7$  on C1 for **6** and **7** and  $-1.4$  on C2 for **6** and  $-0.7$  for **7**. The NPA charge distribution on **6** and **7** was similar to those of bis(methylene)- $\lambda^4$ -sulfanes, which have an isoelectronic relationship with the bis(methylene)- $\lambda^5$ -phosphane anions (Table 1). Considering the aforementioned results in their entirety, it should be concluded that the overall structure of bis(methylene)- $\lambda^5$ -phosphane anion **6** is characterized by not only 3-center-4-electron  $\pi$ -bonds in the C=P=C allene bonding but also a partial contribution of resonance structure **6<sub>A</sub>** rather than **6<sub>B</sub>**.

The  $^{31}\text{P}$  NMR spectra of **6<sub>K</sub>**·(**18-c-6**) in *o*-difluorobenzene and **7<sub>K</sub>**·(**18-c-6**) in benzene-*d*<sub>6</sub> at room temperature showed at 339.0 ppm for **6<sub>K</sub>**·(**18-c-6**) and at 306.8 ppm for **7<sub>K</sub>**·(**18-c-6**), which were significantly low-field shifted compared to that of potassium diphenylphosphide, Ph<sub>2</sub>PK ( $-10.0$  ppm), but slightly high-field shifted compared to that of **1** ( $\delta = 436.5$ ). These chemical shifts thus fall within the reported range for bis(methylene)- $\lambda^5$ -phosphanes (120–347 ppm).<sup>9</sup> The  $^{31}\text{P}$  NMR chemical shifts estimated by the GIAO calculations for **6** (350 ppm) and **7** (317 ppm) are consistent with the experimental results (for details, see the ESI†).<sup>23</sup>

The  $^{13}\text{C}$  NMR spectrum of **6<sub>K</sub>**·(**18-c-6**) in *o*-difluorobenzene at 333 K showed two signals at 75.0 ppm (C1) and 108.1 ppm (C2). These values fall within the reported range for bis(methylene)- $\lambda^5$ -phosphanes (31.6–122.3 ppm).<sup>9</sup> Furthermore, the phosphorus-carbon coupling constants ( $^1J_{\text{C-P}} = 82$  Hz for C1 and 68 Hz for C2) and **7<sub>K</sub>**·(**18-c-6**) ( $^1J_{\text{C-P}} = 74$  Hz for C1 and 44 Hz for C2) are larger than those of previously reported bis(methylene)- $\lambda^5$ -phosphanes (25.6–74.7 Hz), phosphalkenes<sup>27</sup> **V** and (**E**)-**VI** ( $^1J_{\text{C-P}} = 34.5$ –78.1 Hz for  $>\text{C}=\text{P}$ - species), and those of the C–P single bond in **V** and (**E**)-**VI** (Table 1). This result indicates that the C–P bonds in **6<sub>K</sub>**·(**18-c-6**) and **7<sub>K</sub>**·(**18-c-6**) exhibit multiple-bond character with high p-character.

The  $^1\text{H}$  NMR spectrum of **6<sub>K</sub>**·(**18-c-6**) showed that the proton on C2 (6.08 ppm) is significantly high-field shifted compared to



Scheme 5 Protonation of **6<sub>K</sub>** and **7<sub>K</sub>** with *t*-Bu<sub>3</sub>PHBF<sub>4</sub>.

that in **1** (3.72 ppm), indicating an increase in the effect of magnetic anisotropy due to the  $\pi$ -electrons of **6<sub>K</sub>**·(**18-c-6**). The proton on C2 in **7<sub>K</sub>**·(**18-c-6**) could not be observed due to significant overlap with the phenyl protons. The P–H coupling constant in **6**·(**18-c-6**) ( $^2J_{\text{H-P}} = 16.8$  Hz) is larger than that in (Me<sub>3</sub>Si)<sub>2</sub>CHPCl<sub>2</sub> (14.3 Hz) but smaller than those of phosphalkenes **V** and (**E**)-**VI** (18–26 Hz; Table 1).

The UV-vis spectra of **6<sub>K</sub>**·(**18-c-6**) in benzene and **7<sub>K</sub>**·(**18-c-6**) in toluene at room temperature exhibited characteristic absorptions at  $\lambda_{\text{max}} = 378$  nm ( $\epsilon = 7.8 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>) and 474 nm ( $\epsilon = 1.1 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>), respectively. Time-dependent DFT calculations for **6** and **7** showed excitation energies of  $\lambda = 408$  nm and 470 nm (Fig. S13 and S19†), respectively, for the HOMO–LUMO electron transitions ( $\pi$ – $\pi^*$ ), indicating a bathochromic shift due to the  $\pi$ -conjugation of the phenyl group in **7<sub>K</sub>**·(**18-c-6**). Taking these experimental and theoretical investigations into account, it can be concluded that both **6** and **7** contain two C=P  $\pi$ -bonds, *i.e.*, they should behave in solution as bent allene-type compounds with cumulative C=P  $\pi$  bonds.

Finally, reactions of **6<sub>K</sub>**·(**18-c-6**) and **7<sub>K</sub>**·(**18-c-6**) with *t*-Bu<sub>3</sub>PHBF<sub>4</sub> as a protonating reagent were performed to investigate the nucleophilicity/basicity of the allene moieties as indicated by the canonical structures shown in Fig. 4. Both reactions proceeded selectively to produce the corresponding proton adducts **9** and **10** (Scheme 5). Although the anionic charges of **6** and **7** can be expected to be predominantly located on their C1 atoms as resonance structures **6<sub>A</sub>** and **7<sub>A</sub>**, the protonation occurred at their C2 atoms, suggesting that the negative charges on the C1 atoms are significantly stabilized by the double-silyl- $\alpha$ -effect, and thus the C2 atoms should be more basic than the C1 atoms due to their reactive C=P  $\pi$ -bond character. In addition, the theoretical calculations of the products indicated that **9** is thermodynamically more stable than **9'** by  $\Delta E_{\text{Zero}} = 3.4$  kcal mol<sup>-1</sup> (Fig. S47†), which would support the selective formation of the C2-protonated products **9** and **10**.

## Conclusions

In summary, the first isolable bis(methylene)- $\lambda^5$ -phosphane anions (**6<sub>K</sub>**·(**18-c-6**) and **7<sub>K</sub>**·(**18-c-6**)) were synthesized by the desilylation of the corresponding phosphalkene with KHMDS. Spectroscopic and single-crystal X-ray diffraction analyses in combination with theoretical calculations revealed that **6** and **7** show a bent and planar allene structure with two cumulative P=C  $\pi$ -bonds in the C=P=C allene moiety forming a so-called three-center-four-electron  $\pi$ -bond. Further investigations into the reactivity of **6** and **7** are currently in progress in our

Table 1 Comparison of NMR spectral data for **6<sub>K</sub>**·(**18-c-6**) and **7<sub>K</sub>**·(**18-c-6**)

	<b>6<sub>K</sub></b> ·( <b>18-c-6</b> )	<b>7<sub>K</sub></b> ·( <b>18-c-6</b> )	<b>V</b>	( <b>E</b> )- <b>VI</b>
$\delta$ $^{31}\text{P}$	339.0	306.8	326.3, 334.1	256.6
$\delta$ $^{13}\text{C}$				
C1	75.0	72.4	— <sup>a</sup> , 141.2	139.0
( $^1J_{\text{C-P}}$ in Hz)	(82)	(74)	(— <sup>a</sup> , 67)	(54)
C3	108.1	128.0	177.8, 173.2	175.9
( $^1J_{\text{C-P}}$ in Hz)	(68)	(44)	(53, 66)	(35)
C3	—	121.2	—	140.2
( $^1J_{\text{C-P}}$ in Hz)	—	(19)	—	(14)
$\delta$ $^1\text{H}$				
H1	6.08	— <sup>b</sup>	7.89, 7.77	8.21
( $^2J_{\text{H-P}}$ in Hz)	(16.8)	(14.7) <sup>c</sup>	(25, 18)	(26)

<sup>a</sup> Unidentified. <sup>b</sup> Could not be identified due to overlapping. <sup>c</sup>  $^2J_{\text{P-H}}$  in Hz.



laboratories and the results will be disclosed elsewhere in due course.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

The project was designed and conducted by K. S. and T. S. Experimental work such as synthesis and characterization was carried out by A. N. All authors contributed to writing the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- R. Appel, J. Peters and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 80–81.
- R. West, M. J. Fink and J. Michl, *Science*, 1981, **214**, 1343–1344.
- M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587–4589.
- D. R. Taylor, *Chem. Rev.*, 1967, **67**, 317–359.
- R. Appel, E. Gaitzsch, K.-H. Dunker and F. Knoch, *Chem. Ber.*, 1986, **119**, 535–542.
- R. Appel, E. Gaitzsch and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 589–590.
- R. Appel, E. Gaitzsch, K.-H. Dunker and F. Knoch, *Chem. Ber.*, 1986, **119**, 535–542.
- R. Appel, P. Schulte and F. Knoch, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1988, **36**, 147–151.
- P. Becker, H. Brombach, G. David, M. Leuer, H.-J. Metternich and E. Niecke, *Chem. Ber.*, 1992, **125**, 771–782.
- H. J. Metternich and E. Niecke, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 312–313.
- H.-J. Metternich, E. Niecke, J. F. Nixon, R. Bartsch, P. B. Hitchcock and M. F. Meidine, *Chem. Ber.*, 1991, **124**, 1973–1976.
- K. Sugamata, D. Hashizume, Y. Suzuki, T. Sasamori and S. Ishii, *Chem.–Eur. J.*, 2018, **24**, 6922–6926.
- K. Sugamata, Y. Urao and M. Minoura, *Chem. Commun.*, 2019, **55**, 8254–8257.
- K. Sugamata, T. Asakawa, Y. Urao and M. Minoura, *Inorg. Chem.*, 2022, **61**, 17641–17645.
- K. Sugamata and T. Sasamori, *Dalton Trans.*, 2023, **52**, 9882–9892.
- E. Niecke, W. W. Schoeller and D.-A. Wildbrecht, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 131–132.
- E. Niecke, M. Leuer, D.-A. Wildbrecht and W. W. Schoeller, *J. Chem. Soc., Chem. Commun.*, 1983, 1171–1172.
- R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1982, **23**, 2017–2018.
- T. Sasamori and CSD Communication, *Experimental Crystal Structure Determination*, 2024; Compound **1**, DOI: [10.5517/ccdc.csd.cc2l0zg2\(b\)](https://doi.org/10.5517/ccdc.csd.cc2l0zg2(b)) Compound **6<sub>K</sub>**, (18-c-6), DOI: [10.5517/ccdc.csd.cc2l0zh3](https://doi.org/10.5517/ccdc.csd.cc2l0zh3); (c) Compound **7<sub>K</sub>**, (18-c-6), DOI: [10.5517/ccdc.csd.cc2l0zj4](https://doi.org/10.5517/ccdc.csd.cc2l0zj4).
- T. Sasamori, J. M. Villalba Franco, J.-D. Guo, K. Sugamata, S. Nagase, R. Streubel and N. Tokitoh, *Eur. J. Inorg. Chem.*, 2016, **2016**, 678–684.
- K. Sugamata, T. Sasamori and N. Tokitoh, *Chem. Lett.*, 2014, **43**, 95–96.
- K. Issleib, H. Schmidt and C. Wirkner, *Z. Anorg. Allg. Chem.*, 1981, **473**, 85–90.
- (a) Calculated at the B3PW91-D3(bj)/6-311G(3d)//B3PW91-D3(bj)/6-311G(3d) level using the Gaussian 16 program.; (b) NBO calculations were performed using the NBO7 program, see: E. D. Glendening, C. R. Landis and G. Weinhold, *J. Comput. Chem.*, 2019, **40**, 2234–2241.
- A. H. Cowley, R. A. Jones, J. G. Lasch, N. C. Norman, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter and H. M. Zhang, *J. Am. Chem. Soc.*, 1984, **106**, 7015–7020.
- In each reaction leading to the formation of the corresponding bis(methylene)-λ<sup>5</sup>-phosphane anions **6<sub>M</sub>**, the products exhibited extremely low solubility to organic solvent, making it challenging to analyze the product ratios due to the large amounts of insoluble solids in the crude products. Therefore, in all cases, the yields were determined using NMR spectroscopy after purification. The starting material **1** was detected only in entry 3, while in the other reactions, **1** was completely consumed, and no **7<sub>M</sub>** was produced except for entry 1.
- Similar phenyl-group shift from the silicon atom to the carbon atom has been reported, see: (a) I. Fleming, S. K. Patel and C. J. Urch, *J. Chem. Soc., Perkin Trans. 1*, 1989, 115–124; (b) J. J. Eisch, *Ind. Eng. Chem. Prod. Res. Dev.*, 1975, **14**, 11–21.
- R. Appel, J. Menzel, F. Knoch and P. Volz, *Z. Anorg. Allg. Chem.*, 1986, **534**, 100–108.

