Supporting Information for

Bis(methylene)- λ^5 -phosphane Anions

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General Remarks

All manipulations were carried out under an argon atmosphere using either Schlenk line techniques or glove boxes. All solvents were purified by standard methods. Trace amounts of water and oxygen remaining in the solvents were thoroughly removed by bulb-to-bulb distillation from potassium mirror prior to use. All the crystallization was performed at room temperature unless otherwise indicated. ¹H, ¹³C{¹H}, and ²⁹Si{¹H}, ³¹P{¹H}, ³¹P NMR spectra were measured on a Bruker AVANCE-400 spectrometer (¹H: 400 MHz, ¹³C: 101 MHz, ²⁹Si: 79.5 MHz, ³¹P: 162 MHz) and Bruker AVANCE-600 spectrometer (¹³C{¹H}: 151 MHz, ²⁹Si{¹H}: 119 MHz). Signals arising from residual protons CHCl₃(7.26 ppm), C₆D₅H (7.16 ppm) or CDHCl₂(5.32 ppm) and C₆D₆ (128.0 ppm) in C₆D₆ were used as the internal standards for the ¹H and ¹³C NMR spectra. The signal arising from SiMe₄ (0.0 ppm) was used as an external standard for the ²⁹Si NMR spectra. High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-T100LP (DART) mass spectrometer. UV-Vis spectra were recorded on a SHIMADZU UV-3150 UV-Vis-NIR spectrometer under an argon atmosphere in 1 cm quartz cells. All melting points were determined on a Büchi Melting Point Apparatus M-565 and are uncorrected.

Experimental Procedure

·Synthesis of phosphaalkene 1

A solution of $(Ph_2MeSi)_2CBr_2^{S1}$ (3.95 g, 6.97 mmol) in THF (40 mL) and Et₂O (20 mL) at -110 °C was treated with *t*-BuLi (12.0 mL, 1.69 M in pentane, 20.3 mmol). After stirring for 1 min at this temperature, a solution of PCl₃ in Et₂O (4.0 mL, 0.57 M in ether, 2.29 mmol) was added, and the reaction mixture was allowed to warm to room temperature over 1 h. All volatiles were removed under reduced pressure, yielding a crude red oil. The obtained oil was purified by column chromatography (SiO₂, hexane/DCM) to afford an orange oil, which was subsequently reprecipitated to give pure **1** in the form of pale-yellow crystals (615 mg, 0.728 mmol, 31% yield).

1: pale-yellow crystals, Mp. 153–154 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ 0.18 (s, 6H), 0.23 (s, 3H), 0.25 (s, 3H), 3.72 (s, 1H), 6.98 (dd, *J* = 8.2 Hz, *J* = 1.4 Hz, 4H), 7.11 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 4H), 7.15-7.40 (m, 32H); ¹H NMR (400 MHz, C₆D₆) δ 0.31 (s, 6H), 0.46 (s, 3H), 0.47 (s, 3H), 4.00 (s, 1H), 7.05-7.29 (m, 32H), 7.49 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 4H), 7.54-7.59 (m, 4H); ¹³C{¹H} NMR (151 MHz, C₆D₆) δ –1.4 (CH₃), –0.2 (CH₃), 0.9 (CH₃), 1.0 (CH₃), 39.6 (d, *J*_{CP} = 94 Hz, CH), 127.8 (CH), 127.8 (CH), 127.9 (CH), 128.2 (CH), 128.4 (CH), 129.0 (CH), 129.2 (CH), 129.5 (CH), 135.8 (CH), 136.0 (CH), 136.1 (CH), 136.4 (CH), 136.8(C), 137.4 (C), 139.2 (C), 139.6 (C), 178.0 (d, *J*_{CP} = 92 Hz, C); ²⁹Si{¹H} NMR (79.5 MHz, C₆D₆) δ – 19.1 (d, *J*_{SiP} = 11 Hz), –12.4 (d, *J*_{SiP} = 33 Hz), –11.7; ³¹P{¹H} NMR (162 MHz, C₆D₆) δ 436.5 (s); HRMS (DART-positive), *m/z*: Found: 845.3053 ([M+H]⁺), calcd. for C₅₄H₅₃PSi₄ ([M+H]⁺): 845.3040; UV/vis (benzene), 361 nm (ε = 6.1×10²).











Figure S6. UV-vis spectrum of 1 in benzene $(1.9 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1})$ at room temperature.

• Trapping reaction of intermediates of the corresponding lithiated compounds generated by the reaction of $(Ph_2MeSi)_2CBr_2$ with *t*-BuLi



Scheme S1. Trapping reaction of lithiated compounds with MeI.

A mixture of THF (20 mL) and ether (10 mL) solution of $(Ph_2MeSi)_2CBr_2$ (1.98 g, 3.49 mmol) at -110 °C was treated with *t*-BuLi (6.0 mL, 1.69 M in pentane, 10.1 mmol). After 1 min of stirring at this temperature, MeI (1.3 mL, 20.9 mmol) was added, and the reaction mixture was allowed to warm up to room temperature. The volatile materials of the solution were evaporated to afford the crude product. Three methylated compounds **11-13** were assigned to a 1:1:1 generation ratio as judged by the ¹H NMR spectra, as shown Figure S7.



Figure S7. ¹H NMR spectrum of crude product in CDCl₃.

·Synthesis of bis(methylene)- λ^5 -phosphane anion 6_K·(ligand) and 7_K·(ligand)

A mixture of **1** (550 mg, 0.651 mmol) and 18-crown-6 (344 mg, 1.30 mmol) in a J Young Schlenk bottle was dissolved in toluene (5.0 mL) at 45 °C. Then, a toluene solution of KHMDS (1.8 mL, 0.5 M in toluene, 0.9 mmol) was added dropwise, before the reaction mixture was stirred at 45 °C for 90 h. Subsequently, stirring was stopped, and the upper layer was removed. Fresh toluene was added to the flask, resulting in a phase separation; the upper layer was removed, and this procedure was repeated twice, before all volatiles were then removed under reduced pressure. The addition of toluene to the thus obtained residue yielded an orange powder that was reprecipitated to afford bis(methylene)- λ^5 -phosphane anion **6**_K·(**18-c-6**) as a pale yellow solid (183 mg, 0.192 mmol, 30% yield). The filtrate was reprecipitated to afford bis(methylene)- λ^5 -phosphane anion **7**_K·(**18-c-6**) as red crystals (10.3 mg, 0.0124 mmol, 2% yield).

6_K·(**18-c-6**): Mp. 93 °C (dec.). ¹H NMR (400 MHz, *o*-difluorobenzene) δ 0.59 (br, 6H), 0.66(3H), 3.26 (s, 24H), 6.08 (d, $J_{PH} = 16.8$ Hz, 1H), 6.57-7.12 (m, 18H), 7.50-7.55 (m, 4H), 7.99 (br, 8H); ¹³C{¹H} NMR (151 MHz, *o*-difluorobenzene, 333 K) δ –1.4 (d, $J_{CP} = 14$ Hz, CH₃), 3.1 (d, $J_{CP} = 10$ Hz, CH₃), 70.1 (CH₂), 75.0 (d, $J_{CP} = 82$ Hz, C), 108.1 (d, $J_{CP} = 68$ Hz, CH), 126.8 (CH), 126.9 (CH), 127.0 (CH), 135.4(CH), 136.5(CH), 145.7(C), 145.8(C); ²⁹Si{¹H} NMR (79.5 MHz, C₆D₆) δ –16.5, –16.0; ³¹P{¹H} NMR (162 MHz, *o*-difluorobenzene) δ 339.0 (s); HRMS(DART-negative), *m/z*: Found: 647.2190 ([**6**_K]⁻), calcd. For C₄₁H₄₀PSi₃ ([**6**_K]⁻): 647.2175; UV/vis (benzene), 378 nm (ε = 7.8×10³).





¹H NMR spectrum of 6_{K} (18-c-6) in *o*-difluorobenzene. (*toluene)



Figure S9. ¹³C{¹H} NMR spectrum of 6_{K} ·(18-c-6) in *o*-difluorobenzene.







Figure S11. ${}^{31}P{}^{1}H$ NMR spectrum of 6_{K} ·(18-c-6) in *o*-difluorobenzene.





VT-NMR spectra for 6_{K} (18-c-6) in *o*-difluorobenzene. (*toluene)



Figure S13. UV-vis spectrum of **6**_K·(**18-c-6**) in benzene ($1.6 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) at room temperature. 7_K·(**18-c-6**): Mp. 53 °C (dec.). ¹H NMR (400 MHz, C₆D₆) δ 0.94 (s, 6H), 2.96 (s, 24H), 6.41 (t, *J* = 7.4 Hz, 1H), 6.85 (dd, *J* = 7.4 Hz, *J* = 7.4 Hz, 2H), 7.21-7.32 (m, 15H), 8.10 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 8H); ¹³C{¹H} NMR (151 MHz, C₆D₆, 333 K) δ 3.2 (d, *J*_{CP} = 8 Hz, CH₃), 70.1 (CH₂), 72.4 (d, *J*_{CP} = 74 Hz, C), 116.4 (CH), 121.2 (d, *J*_{CP} = 18 Hz, CH), 127.2 (CH), 127.4 (CH), 128.0 (d, *J*_{CP} = 44 Hz, CH), 128.4 (CH), 136.6 (CH), 145.3 (C), 150.4 (d, *J*_{CP} = 24 Hz, C); ²⁹Si{¹H} NMR (79.5 MHz, *o*-difluorobenzene) δ –15.0 (d, *J*_{SiP} = 21 Hz); ³¹P NMR (162 MHz, C₆D₆) δ 306.8 (d, *J*_{PH} = 14.7 Hz); UV/vis (toluene), 474 nm (ε = 1.1×10^4).





¹H NMR spectrum of 7_{K} (18-c-6) in C₆D₆. (*hexane/o-defluorobenzene)





¹³C{¹H} NMR spectrum of 7_{K} ·(18-c-6) in C₆D₆.



Figure S16. ²⁹Si{¹H} NMR spectrum of 7_{K} ·(18-c-6) in *o*-difluorobenzene.







VT-NMR spectra for 7_{K} (18-c-6) in C₆D₆. (*hexane)



Figure S19. UV-vis spectrum of $7_{\rm K}$ in toluene $(1.0 \times 10^{-4} \, {\rm mol} \cdot {\rm L}^{-1})$ at room temperature.

·Synthesis of bis(methylene)- λ^5 -phosphane anion 6_K ·(cryptand)

A mixture of **1** (103 mg, 0.122 mmol) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexaoxane (47.3 mg, 0.126 mmol) in a J Young Schlenk bottle was dissolved in toluene (1.0 mL) at 45 °C. Then, a toluene solution of KHMDS (0.4 mL, 0.5 M in toluene, 0.2 mmol) was added dropwise, and the reaction mixture was stirred at 45 °C for 6 d. Then, stirring was stopped, and the upper layer was removed. Fresh toluene was added to the flask, leading to a phase separation; the upper layer was removed, and this procedure was repeated three times. Then, all volatiles were then removed under reduced pressure, yielding a dark-red oil containing the bis(methylene)- λ^5 -phosphane anion **6**_K·(**cryptand**) (156 mg, 96% yield judging from the ¹H NMR spectrum).

6_K·(**cryptand**): ¹H NMR (400 MHz, *o*-difluorobenzene) δ 0.56 (br, 6H), 0.66(3H), 2.17 (t, J = 4.4 Hz, 12H), 3.15 (t, J = 4.4 Hz, 12 H), 3.20 (s, 12H), 6.05 (d, $J_{PH} = 16.8$ Hz, 1H), 6.56-7.11 (m, 18H), 7.48-7.54 (m, 4H), 7.98 (br, 8H); ¹³C {¹H} NMR (151 MHz, *o*-difluorobenzene, 333 K) δ –1.4 (d, $J_{CP} = 14$ Hz, CH₃), 3.2 (d, $J_{CP} = 10$ Hz, CH₃), 54.1 (CH₂), 67.7 (CH₂), 70.5 (CH₂), 74.8 (d, $J_{CP} = 83$ Hz, C), 108.0 (d, $J_{CP} = 69$ Hz, CH), 126.8 (CH), 126.9 (CH), 127.0 (CH), 135.4 (CH), 136. 5 (CH), 145.6(C), 145.8 (C); ²⁹Si {¹H} NMR (79.5 MHz, *o*-difluorobenzene) δ –16.6, –16.1; ³¹P {¹H} NMR (162 MHz, *o*-difluorobenzene) δ 338.8 (s).



Figure S20. ¹H NMR spectrum of 6_{K} (cryptand) in *o*-difluorobenzene. (*KHMDS)



Figure S21. ¹³C{¹H} NMR spectrum of 6_{K} (cryptand) in *o*-diffuorobenzene. (*KHMDS)



Figure S22. ²⁹Si{¹H} NMR spectrum of 6_{K} (cryptand) in *o*-difluorobenzene.



Figure S23. ${}^{31}P{}^{1}H$ NMR spectrum of 6_{K} (cryptand) in *o*-difluorobenzene.

• Synthesis of bis(methylene)-λ⁵-phosphane anion 6_{Li}·(12-c-4)

To a mixture of **1** (112 mg, 0.132 mmol) and 12-crown-4 (0.08 mL, 0.5 mmol) in a J Young Schlenk bottle was added toluene (1.0 mL) at 60 °C. Then, a toluene solution of LiHMDS (0.4 mL, 1 M in toluene, 0.4 mmol) was added dropwise, and the solution was stirred at 60 °C for 8 d to form a pale-yellow precipitate that was isolated by decantation. The solids were washed four time with toluene, before all volatiles were removed under reduced pressure to yield bis(methylene)- λ^5 -phosphane anion 6_{Li} ·(12-c-4) (16.4 mg, 0.0163 mmol, 12% yield) as a pale-yellow solid.

6_{Li}·(**12-c-4**): ¹H NMR (400 MHz, *o*-difluorobenzene) δ 0.57 (br, 6H), 0.67(3H), 3.33 (s, 32H), 6.09 (d, $J_{PH} = 17.2$ Hz, 1H), 6.55-7.12 (m, 18H), 7.50-7.56 (m, 4H), 7.99 (br, 8H); ¹³C {¹H} NMR (151 MHz, *o*-difluorobenzene, 333 K) δ –1.5 (d, $J_{CP} = 14$ Hz, CH₃), 3.2 (d, $J_{CP} = 9$ Hz, CH₃), 67.3 (CH₂), 75.1 (d, $J_{CP} = 82$ Hz, C), 107.9 (d, $J_{CP} = 69$ Hz, CH), 126.8 (CH), 126.9(CH), 127.0 (CH), 127.1 (CH), 135.4 (CH), 136.5 (CH), 145.6 (C), 145.7 (C); ²⁹Si {¹H} NMR (79.5 MHz, *o*-difluorobenzene) δ – 16.6, -16.0; ³¹P {¹H} NMR (162 MHz, C₆D₆) δ 338.8 (s); HRMS(DART-negative), *m/z*: Found: 647.2149 ([**6**_{Li}]⁻), calcd. For C₄₁H₄₀PSi₃ ([**6**_{Li}]⁻): 647.2175





¹H NMR spectrum of 6_{Li} ·(12-c-4) in *o*-difluorobenzene.



Figure S25. ¹³C{¹H} NMR spectrum of 6_{Li} ·(12-c-4) in *o*-difluorobenzene.





²⁹Si NMR spectrum of 6_{Li} ·(12-c-4) in *o*-difluorobenzene.



Figure S27. ${}^{31}P{}^{1}H$ NMR spectrum of $6_{Li} \cdot (12-c-4)$ in *o*-difluorobenzene.

·Synthesis of bis(methylene)- λ^5 -phosphane anion 6_{Na}·(18-c-6)

A mixture of **1** (106 mg, 0.125 mmol) and 18-crown-6 (67.3 mg, 0.255 mmol) was dissolved in toluene (1.0 mL) in a J Young Schlenk bottle at 60 °C. Then, a toluene solution of NaHMDS (0.4 mL, 0.6 M in toluene, 0.2 mmol) was added dropwise to the flask, and the reaction mixture was stirred at 60 °C for 3 d. Subsequently, stirring was stopped, and the upper layer was removed. Fresh toluene was added to the flask, resulting in a phase separation; the upper layer was removed, and this procedure was repeated five times, before all volatiles were then removed under reduced pressure to yield bis(methylene)- λ^5 -

phosphane anion 6_{Na} (18-c-6) (90.4 mg, 77%) as a dark-red oil.

6_{Na}·(**18-c-6**): ¹H NMR (400 MHz, *o*-difluorobenzene) δ 0.58 (br, 6H), 0.65(3H), 3.28 (s, 24H), 6.06 (d, J_{PH} = 16.8 Hz, 1H), 6.48-7.11 (m, 18H), 7.48-7.52 (m, 4H), 7.98 (br, 8H); ¹³C{¹H} NMR (151 MHz, *o*-difluorobenzene, 333 K) δ –1.5 (d, J_{CP} = 14 Hz, CH₃), 3.2 (d, J_{CP} = 9 Hz, CH₃), 68.9 (CH₂), 75.0 (d, J_{CP} = 84 Hz, C), 108.0 (d, J_{CP} = 69 Hz, CH), 126.8 (CH), 126.9(CH), 127.0 (CH), 127.1 (CH), 135.4 (CH), 136.5 (CH), 145.6 (C), 145.7 (C) ; ²⁹Si{¹H} NMR (79.5 MHz, *o*-difluorobenzene) δ – 16.6, -16.0; ³¹P{¹H} NMR (162 MHz, C₆D₆) δ 338.7 (s); HRMS(DART-negative), *m/z*: Found: 647.2149 ([**6**_{Na}]⁻), calcd. For C₄₁H₄₀PSi₃ ([**6**_{Na}]⁻): 647.2175.



Figure S29. ¹³C{¹H} NMR spectrum of 6_{Na} ·(18-c-6) in *o*-difluorobenzene.







Figure S31. 31 P NMR spectrum of 6_{Na} ·(18-c-6) in *o*-difluorobenzene.

·Reaction of 1 with *t*-BuOK

To a mixture of compound 1 (109 mg, 0.129 mmol), 18-crown-6 (68.4 mg, 0.259 mmol), and *t*-BuOK (21.5 mg, 0.192 mmol) in a J Young Schlenk bottle was added toluene (1.0 mL) at 45 °C. The solution was stirred at same temperature for 43.5 h to form pale yellow precipitates, which was isolated by the decantation. The solids were washed twice with toluene, and all volatiles were removed under reduced pressure, yielding a pale yellow solid (78.2 mg).





¹H NMR spectrum of the crude product in C_6D_6 .



Figure S33. ³¹P NMR spectrum of the toluene supernatant.

·Reaction of 6_K·(18-c-6) with *t*-Bu₃PHBF₄

A benzene (1 mL) solution of $6K \cdot (18\text{-c-6})$ (54.8 mg, 0.0576 mmol) in a glass bottle was treated with *t*-Bu₃PHBF₄ (17.8 mg, 0.0614 mmol) at room temperature. After 3 h of stirring at this temperature, the mixture was filtered through a pad of Celite, before all volatiles were removed under reduced pressure to yield proton-adduct **9** as a pale-yellow oil (39.7 mg).

9: ¹H NMR (400 MHz, C₆D₆) δ 0.43 (s, 3H), 0.50 (s, 3H), 0.62 (s, 3H), 2.32 (d, *J* = 2.4 Hz, 2H), 7.06-7.22 (m, 18H), 7.31(ddd, *J* = 6.0 Hz, *J* = 1.6 Hz, *J* = 1.6 Hz, 4H), 7.41 (ddd, *J* = 6.0 Hz, *J* = 2.0 Hz, 4H), 7.58 (ddd, *J* = 5.2 Hz, *J* = 2.0 Hz, *J* = 2.0 Hz, 4H); ¹³C{¹H} NMR (101 MHz, C₆D₆) δ -2.8 (d, *J*_{CP} = 4 Hz, CH₃), -0.1 (d, *J*_{CP} = 12 Hz, CH₃), 1.23 (CH₃), 33.3 (d, *J*_{CP} = 73 Hz, CH₂), 127.9 (CH), 128.1 (CH), 128.2 (CH), 128.6 (CH), 129.3 (CH), 129.6 (CH), 135.2 (CH), 135.5 (CH), 135.8 (CH), 136.6 (C), 138.1 (C), 138.2 (C), 187.8 (d, *J*_{CP} = 89 Hz, C); ²⁹Si{¹H} NMR (79.5 MHz, C₆D₆) δ -43.3, -18.2 (d, *J*_{SiP} = 11 Hz), -9.6 (d, *J*_{SiP} = 9 Hz); ³¹P{¹H} NMR (162 MHz, C₆D₆) δ 427.0 (s); HRMS(DART-positive), *m/z*: Found: 649.2321 ([**9**+H]⁺), calcd. For C₄₁H₄₁PSi₃ ([**9**+H]⁺): 649.2332.



Figure S34. ¹H NMR spectrum of 9 in C_6D_6 . (*K⁺(18-c-6)·BF₄^{-/}(*t*-Bu)₃P)





Figure S36. 29 Si{¹H} NMR spectrum of 9 in C₆D₆.



·Reaction of 7_K·(18-c-6) with *t*-Bu₃PHBF₄

A benzene (0.5 mL) solution of 7_{K} ·(18-c-6) (22.1 mg, 0.026 mmol) in a glass bottle was treated with *t*-Bu₃PHBF₄ (7.7 mg, 0.026 mmol) at room temperature. After stirring at this temperature for 17 h, the mixture was filtered through a pad of Celite, before all volatiles were removed under reduced pressure to yield proton-adduct 10 as a pale-yellow oil (13.2 mg).

10: ¹H NMR (400 MHz, C₆D₆) δ 0.58 (s, 3H), 0.70 (s, 3H), 3.35 (d, *J* = 3.6 Hz, 2H), 6.73 (d, *J* = 6.8 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 7.00 (dddd, *J* = 7.3 Hz, *J* = 7.3 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz, 2H), 7.12-7.18 (m, 12H), 7.52 (ddd, *J* = 5.6 Hz, *J* = 2.0 Hz, *J* = 2.0 Hz) 4H), 7.59-7.62 (m, 4H); ¹³C{¹H} NMR (101 MHz, C₆D₆) δ -0.4 (d, *J*_{CP} = 13 Hz, CH₃), 1.5 (CH₃), 48.5 (d, *J*_{CP} = 58 Hz, CH₂), 126.1 (CH), 128.0 (CH), 128.2 (CH), 128.6(CH), 129.0 (CH), 129.3 (d, *J*_{CP} = 5 Hz, CH), 129.5 (d, *J*_{CP} = 7 Hz, CH), 135.5 (CH), 135.8 (CH), 137.4 (d, *J*_{CP} = 7 Hz, C), 137.7 (C), 138.1 (d, *J*_{CP} = 9 Hz, C), 191.6 (d, *J*_{CP} = 90 Hz, C) ; ²⁹Si{¹H} NMR (119 MHz, C₆D₆) δ -17.5 (d, *J*_{SiP} = 10 Hz), -9.8 (d, *J*_{SiP} = 33 Hz) ; ³¹P{¹H} NMR (162 MHz, C₆D₆) δ 427.7 (s) ; HRMS(DART-positive), *m/z*: Found: 546.1926 ([**10**+H₂O]⁺), calcd. For C₃₄H₃₅OPSi₂ ([**10**+H₂O]⁺): 546.1964.





¹H NMR spectrum of **10** in C₆D₆. (*K⁺(18-c-6)·BF₄^{-/}(*t*-Bu)₃P)







Figure S41. ${}^{31}P$ NMR spectrum of 10 in C₆D₆.

X-Ray Crystallographic Analysis

Single crystals of 1, $6_{K} \cdot (18\text{-c-6})$, and $7_{K} \cdot (18\text{-c-6})$ were obtained after recrystallization from toluene/hexane (1), benzene ($6_{K} \cdot (18\text{-c-6})$), or toluene/pentane ($6_{K} \cdot (18\text{-c-6})$) at room temperature. Intensity data of 1 and $6_{K} \cdot (18\text{-c-6})$ were collected on a Bruker APEX-II system using Mo-K α radiation ($\lambda = 0.71073$ Å), while those of $6_{K} \cdot (18\text{-c-6})$ were collected on the BL02B1 beamline of SPring-8 (proposal numbers: 2023A1539, 2023A1771, 2023A1785, 2023A1794, 2023A1859, 2023A1925, 2023B1675, 2023B1806, 2023B1878, and 2024A1857) on a PILATUS3 X CdTe 1M camera using synchrotron radiation ($\lambda = 0.4132$ Å). The structures were solved using SHELXT-2018^{S2} and refined by a full-matrix least-squares method (LSQ) on F² for all reflections using SHELXL-2018^{S3} and the Yadokari-XG software package.^{S4} All non-hydrogen atoms were refined anisotropically, while the positions of all hydrogen atoms were calculated geometrically and refined as riding models. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-2384224 (1), 2384225 ($6_{K} \cdot (18\text{-c-6})$), and 2384226 ($6_{K} \cdot (18\text{-c-6})$); these can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request.cif</u>.

Compound	1	6 _K ·(18-c-6)	7 _K ·(18-c-6)
Formula	C54H53PSi4	C ₆₅ H ₇₆ KO ₆ PSi ₃	C46H56KO6PSi2
Molecular Weight	845.29	1107.59	831.15
Temperature / K	103	103	100
λ (Å)	0.71073	0.71073	0.4132
Crystal size / mm ³	0.200×0.150×0.100	0.120×0.060×0.030	0.100×0.050×0.020
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i> (#15)	P-1 (#2)	P-1 (#2)
<i>a</i> /Å	40.2431(4)	12.27460(10)	11.2805(2)
b /Å	10.30930(10)	12.7930(2)	15.6436(3)
c /Å	22.5509(2)	20.8875(2)	26.8108(4)
α/deg	90	80.77420(10)	87.8780(10)
β / deg	95.1220(10)	79.2490(10)	83.365(2)
γ / deg	90	73.9750(10)	71.306(2)
$V/Å^3$	9318.52(15)	3076.30(6)	4451.62(14)
Ζ	8	2	4
μ / mm ⁻¹	0.198	0.220	0.069
$D_{ m calcd.}$ / g·cm ⁻³	1.205	1.196	1.240
$ heta_{ m max}$	27.500	29.148	15.773
Refl./restr./param.	10678/0/532	15529/0/989	21179/319/1180
Completeness	99.8	99.8	99.7
GOF	1.112	1.026	1.065
R_1 (I>2 σ (I))	0.0633	0.0310	0.0707
wR_2 (I>2 σ (I))	0.1705	0.0801	0.1752
R_1 (all data)	0.0673	0.0350	0.0802
wR_2 (all data)	0.1741	0.0826	0.1803
Largest diff. peak and hole /e·Å ⁻³	1.143, -0.681	0.410, -0.212	0.597, -0.470
CCDC DOI:	10.5517/ccdc.csd.cc2l0zg2	10.5517/ccdc.csd.cc2l0zh3	10.5517/ccdc.csd.cc2l0zj4

Table S1. Crystal data and data collection of 1, 6_{K} (18-c-6), and 6_{K} (18-c-6).





Theoretical Calculations

Theoretical calculations for the geometry optimization and frequency calculations of **1**, 6_{K} ·(**18-c-6**), **6**, **7**, **8**, **9**, **9**', and model compounds (*cf.* Table S1) were carried out using the Gaussian 16 (Revision B.01 and C.01) program package.^{S5} Geometry optimizations were performed at the B3PW91-D3(BJ) level using basis sets of 6-311G(3d) for P, Si, C, and H. Minimum energies for the optimized structures were confirmed by frequency calculations. GIAO calculations were performed at the GIAO-B3PW91-D3(BJ) level using basis sets of 6-311G(3d) for P, Si, C, and H. Minimum energies for the optimized structures were confirmed by frequency calculations. GIAO calculations were performed at the optimized structures were confirmed by frequency calculations. Energies were corrected for the zero-point energy (ZPE) term at the optimization level (E_{zero}). Computational time was generously provided by the Supercomputer Laboratory at the Institute for Chemical Research (Kyoto University). Computations were also carried out using resources of the Research Center for Computational Science, Okazaki, Japan (Projects: 24-IMS-C377/24-IMS-C397). The coordinates of the optimized structures are included in the corresponding .xyz files as supporting information.



Figure S43.Optimized structure of 6_{K} .(18-c-6).Table S2. Experimental and calculated values of the bond parameters for 6_{K} .(18-c-6).

	Experimental values (Å, deg)	Calculated values (Å, deg)
P1-C1	1.723(1)	1.724
P1-C2	1.694(1)	1.683
C1–Si1	1.8200(9)	1.810

C1–Si2	1.832(1)	1.829
C2–Si3	1.813(1)	1.812
C1–P1–C2	112.23(5)	111.8



Figure S44.	Optimized structure of 6 .
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Table S2. Experimental	l and calculated	values of the	bond parameters	for 6 .
1			1	

Table S2. Experimental and calculated values of the bond parameters for 6.					
Experimental values (Å, deg) Calculated values (Å, deg)					
P1-C1	1.723(1)	1.726			
P1-C2	1.694(1)	1.687			
C1–Si1	1.8200(9)	1.805			
C1–Si2	1.832(1)	1.817			
C2–Si3	1.813(1)	1.805			
C1–P1–C2	112.23(5)	110.3			



Figure S45.Optimized structure of 7.

Table S3. Experimenta	l and calculated valu	ues of the bond	parameters for 7.
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	Experimental values (Å, deg)	Calculated values (Å, deg)
P1C1	1.717(2)	1.729
P1C2	1.690(3)	1.698
C1–Si1	1.818(3)	1.808
C1–Si2	1.827(3)	1.818
C1-P1-C2	112.6(1)	109.9



R

R	Н (6)	Me	SiMe ₃	SiMe ₂ Ph (8)	Figure S46.
θ (°)	110.27	115.96	123.50	114.01	tructura
φ (deg)	2.55	19.19	42.67	61.62	1
					compar

isons of bis(methylene)- λ^5 -phosphane anions.



Compound	9	9'	Figure S47.
ΔE_{Zero} (a.u.)	-2796.205298	-2796.199865	elative
ΔE_{Zero} (kcal·mol ⁻¹)	-3.4	0	energy
Zero-point correction (a.u.)	0.693336	0.692410	between
Thermal correction to Gibbs Free Energy (a.u.)	0.610604	0.608531	proton-
			adducts 9

and 9'.

Natural-Resonance-Theory (NRT) calculations ^{S6}

To show the contributions of the considerable canonical structures of a bis(methylene)- λ^5 -phosphane anion for the readers, we carried out the Natural Resonance Theory (NRT) calculations using H- and H₃Si- substituted model compounds V and VI, respectively. NRT analysis revealed two degenerate resonance structures derived from C-anionic structures for compound V (each contributing 46%) as shown in Figure S48. In contrast, VI exhibited four degenerate anion-delocalized resonance contributors, with an NRT weight of 6.4% each (totaling approximately 25%), and two degenerate C-anionic-type structures, with an NRT weight of 11.1% each (totaling 22%) (Figure S49). On the basis of the results of NRT calculations, the silyl substituents would stabilize the π -electron/negative charge delocalized electronic structure, which cause the spreading π -conjugation. On the consideration of the sum of resonance structures with the highly π -electron delocalized canonical structures, we can conclude that the obtained bis(methylene)- λ^5 -phosphane anions **6** and **7** should exhibit the allene-type electronic structures with C=P=C cumulative π -bonds by delocalizing the negative charge through Si-hyperconjugation.

Compound V





Resonance contributors of H-substituted model compound V.





Estimation for ³¹P NMR chemical shifts

All calculated ³¹P shielding constants σ_{calc} were converted to ³¹P NMR chemical shifts δ_{calc} (ppm, 85% aqueous solution of H₃PO₄) using Eq. (1),

$$\delta_{\text{calc}} = \sigma_{\text{calc}}(\text{PMe}_3) - \sigma_{\text{calc}} - 62 \text{ ppm}$$
(1)

where $\sigma_{calc}(PMe_3)$ is the absolute ³¹P NMR shielding constant of trimethylphosphine (PMe₃) calculated at the same level of theory.

Estimation of the rotation barriers for 6a and 7a



Figure S50.Activation barriers (kcal mol⁻¹) for the rotation of the C=P bond in bis(methylene)- λ^5 -phosphane anions6a and 7a. Geometric optimizations were carried out at the B3PW91-D3(BJ)/6-31G(d) level.

The ¹H NMR spectra of $6_{K} \cdot (18-c-6)$ in *o*-difluorobenzene at room temperature showed a highly broadened signal for the (Ph₂MeSi)₂C= moiety, which coalesced into one signal upon heating to 343 K (Figure S12), suggesting restricted rotation around the C1=P1 bond at room temperature similar to other bis(methylene)- λ^4 -chalcogenanes. Comparable VT-NMR behavior was observed in the ¹H NMR spectra of $7_{K} \cdot (18-c-6)$ in C_6D_6 (Figure S18). Theoretical calculations for model compounds **6a** and **7a**, which bear Me₃Si groups instead of Ph₂MeSi groups, suggested rotation barriers of 16.0 kcal·mol⁻¹ and 15.6 kcal·mol⁻¹ for their C1=P1 bonds, and 26.3 kcal·mol⁻¹ and 21.8 kcal·mol⁻¹ for their P1=C2 bonds, respectively. These results suggest that the C1=P1 bond can rotate slowly, even at room temperature (Figure S50). The smaller rotation barriers of the P1=C1 bonds in **6a** and **7a** relative to those of P1=C2 also support the unsymmetric contribution of the resonance structures **6**_A and **7**_A (Fig. 4). These rotation barriers are almost similar to those of the C=S bonds in previously reported bis(methylene)- λ^4 -sulfanes.

Theoretical calculations were carried out at the B3PW91-D3(bj)/6-31G(d) level for model compounds **6a** and **7a**, which contain Me₃Si groups instead of Ph₂MeSi groups. All calculations included the solvent effect with the scrf method. The data for *o*-difluorobenzene for the calculations are shown in table S4. To locate the transition-state structures, the synchronous transit-guided quasi-Newton (STQN) method was employed in Gaussian using the QST3 keywords. After identifying the predicted transition-state structures, these structures were further optimized using the eigenvector-following method with the Opt=TS keywords. Finally, an internal-reaction-coordinate (IRC) calculation was performed. Activation barriers were estimated as the energy differences between transition states (TS) and the grand state of products (PR) and

starting materials (SM). These calculations provided the energy diagram for the rotation barriers of **6a** and **7a** as shown in Figure S48.

Table S4

o-difluorobenzene	Eps	Epsinf	R_{Solv}	Density	Eps=x:
MW: 114.09, D = 1.16 g/mL	13.8	2.082	3.99	0.006125	Specifi

the

es

static (or zero-frequency) dielectric constant of the solvent.

EpsInf=x: Specifies the dynamic (or optical) dielectric constant of the solvent.

R_{Solv}=x: Specifies the solvent radius (in Angstroms).

Density=x: Density: 1.16 g/mL Indeed, if ρ , D, and MW to be density in g/mL, density in particle/Å³,

and molecular weight in *gr/mol* of the desirable solvent, then: $D = \rho/(1.66 \times MW)$.



Figure S51. Structure of a transition state between 6a and Pr1 with a negative frequency of -122.2623 and its IRC path.



Figure S52. Structure of a transition state between 6a and Pr2 with a negative frequency of -688.7312 and its IRC



Figure S53.Structure of a transition state between 7a and Pr1 with a negative frequency of -141.4047 and its IRC





Figure S54. Structure of a transition state between 7a and Pr2 with a negative frequency of -473.7128 and its IRC path.

·Comparison of ΔE_{ZERO} between the desilylation and deprotonation reaction of 1.

To investigate the reaction mechanism for desilylation reaction, we performed theoretical calculations on the potential energy surface of both a deprotonation reaction (upper) and a desilylation reaction of the phosphaalekene (SM) as showns in Figure S55. The reaction barrier for the deprotonation product via TS1 is smaller than that of desilylation product via TS2, while the product of desilylation reaction (**Pr2**) is significantly stable compared to that of deprotonation reaction (**Pr1**). As the result, it was found that the formation of bis(methylene)- λ^5 -phosphane anion 6 is thermodynamically favored reactions.



Figure S55. DFT-derived energy diagram for the desilylation and the deprotonation pathways, calculated at the B3PW91-D3(BJ)/6-31G(d) level.

·Atom-in-molecules analyses of bis(methylene)- λ^5 -phosphane anions and bis(methylene)- λ^4 -sulfanes.

Topological analysis of the electron density was performed in MultiWFN (version 3.7).⁸⁷ Bond paths and bond critical point were visualized in VMD.⁸⁸

As a result of the atoms-in-molecule (AIM) analysis of compound 6, the C—P bonds are characterized by a positive electron density (ρ_{BCP}): 0.136 eÅ⁻³ for C2—P1 and 0.142 eÅ⁻³ for C4—P1, as well as a small positive Laplacian ($\nabla^2 \rho_{BCP}$): 0.774 eÅ⁻⁵ for C2—P1 and 0.629 eÅ⁻⁵ for C4—P1 at the bond critical points (BCPs). The bond ellipticity at the BCP of the C—P bonds was 0.070 for C2—P1 and 0.021 for P1—C4. For comparison, the corresponding parameter for the C—C bond in a benzene ring ranges from 0.23 to 0.28, while for a C—Si single bond, it ranges from 0.0063 to 0.013. The AIM analysis of compound 7 reveals similar characteristics: the C—P bonds display a positive electron density (ρ_{BCP}): 0.139 e⁻Å⁻³ for C3—P1 and 0.136 e⁻Å⁻³ for P1—C2, along with a small positive Laplacian ($\nabla^2 \rho_{BCP}$): 0.734 e⁻Å⁻⁵ for C2—P1 and 0.619 eÅ⁻⁵ for C4—P1 at the BCPs. The bond ellipticity at the BCP of the C—P bonds was 0.040 for C2—P1 and 0.037 for P1—C4. In contrast, the bond ellipticities at the BCPs of C—S bonds (ranging from 0.18 to 0.24) in bis(methylene)- λ^4 -sulfanes VII and VIII indicate significant π -bonding character (Figures S56–S59). Furthermore, we performed an AIM analysis of phosphaalkene 1. The bond ellipticities of 1 were 0.199 for the C–P single bond and 0.0397 for the C=P double bond (Figure S60).



Connected atoms: 4(C) - 1(P)Density of all electrons: 0.1359135694E+00Laplacian of electron density: 0.6288015752E+00Ellipticity of electron density: 0.020897------CP 151, Type (3,-1) -------Connected atoms: 1(P) - 2(C)Density of all electrons: 0.1417925052E+00Laplacian of electron density: 0.7744746184E+00Ellipticity of electron density: 0.069699

Figure S56. Bond critical points of C-P-C moiety and bond paths in 6, calculated at the B3PW91-D3(BJ)/6-311G(d) level.



------ CP 121, Type (3,-1) ------Connected atoms: 3(C) -- 1(P) Density of all electrons: 0.1394148130E+00 Laplacian of electron density: 0.7338981765E+00 Ellipticity of electron density: 0.039732 ------ CP 122, Type (3,-1) ------Connected atoms: 1(P) -- 2(C) Density of all electrons: 0.1357569866E+00 Laplacian of electron density: 0.6185441366E+00 Ellipticity of electron density: 0.037437

Figure S57.Bond critical points of C-P-C moiety and bond paths in 7, calculated at the B3PW91-D3(BJ)/6-311G(d)

level.





------ CP 116, Type (3,-1) ------Connected atoms: 1(S) -- 3(C) Density of all electrons: 0.1806611520E+00 Laplacian of electron density: 0.6438772010E+00 Ellipticity of electron density: 0.180875 ------ CP 120, Type (3,-1) ------Connected atoms: 1(S) -- 2(C) Density of all electrons: 0.1811393839E+00 Laplacian of electron density: 0.5378007380E+00 Ellipticity of electron density: 0.237114

Figure S59.Bond critical points and bond paths of C-S-C moiety in bis(methylene)-λ-sulfane VIII, calculated at the
B3PW91-D3(BJ)/6-311G(d) level.



------ CP 209, Type (3,-1) ------Connected atoms: 1(P) -- 2(C)Density of all electrons: 0.1468366327E+00Laplacian of electron density: 0.8286015272E+00Ellipticity of electron density: 0.099304------ CP 210, Type (3,-1) ------Connected atoms: 1(P) -- 3(C)Density of all electrons: 0.1225423953E+00Laplacian of electron density: 0.3255458106E+00Ellipticity of electron density: 0.198677

Figure S60. Bond critical points and bond paths of C-P-C moiety in phosphaalkene 1, calculated at the B3PW91-D3(BJ)/6-311G(d) level.

References

- S1) A. Inoue, J. Kondo, H. Shinokubo, K. Oshima, Chem. Lett. 2001, 30, 956–957.
- S2) G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8.
- S3) G. M. Sheldrick, Acta Cryst., 2015, C71, 3-8.
- S4) Wakita, K. (2001). Yadokari-XG. Software for Crystal Structure Analyses. Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, Kabuto, C., Akine, S., Nemoto, T. and Kwon, E. J. Cryst. Soc. Jpn., 2009, 51, 218-224.
- S5) Gaussian 16, Revision B.01 and C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
- S6) NBO7 program: E. D. Glendening, C.R. Landis and G. Weinhold, J. Comput. Chem. 2019, 40, 2234-2241.
- S7) MultiWFM program: T. Lu, J. Chem. Phys., 2024, 161, 082503.
- S8) VMD: program: W. Humphrey, A. Dalke and K. Schulten, J. Mol. Graph., 1996, 14, 33-8, 27-8.