

Supporting Information

[4+2] Cycloaddition of 9-Anthryldiphosphene with Electron-deficient Olefins: Transformation of a Diaryldiphosphene to Alkylaryldiphosphenes

*Akihiro Tsurusaki, Takahiro Sasamori, and Norihiro Tokitoh**

Institute for Chemical Research, Kyoto University, Gakasho, Uji, Kyoto 611-0011 (Japan)

To whom correspondence should be addressed. Phone: +81-774-38-3200. Fax: +81-774-38-3209. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp.

Experimental Section

General Procedures. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified by The Ultimate Solvent System (Glass Contour Company).^{S1} Benzene-*d*₆ and cyclohexane-*d*₁₂ used in the spectroscopy were dried by using a potassium mirror. The ¹H NMR (400 or 300 MHz) and ¹³C NMR (100 or 75 MHz) spectra were measured in C₆D₆, C₆D₁₂, or CDCl₃ with a JEOL JNM AL-400 or AL-300 spectrometer. Signals due to C₆D₅H (7.15 ppm), C₆D₁₁H (1.38 ppm), and CHCl₃ (7.25 ppm) in ¹H NMR and those due to C₆D₆ (128 ppm), C₆D₁₂ (26.4 ppm), and CDCl₃ (77.0 ppm) in ¹³C NMR were used as internal references, respectively. The ³¹P NMR (121 MHz) spectra were measured in C₆D₆ with a JEOL AL-300 spectrometer using 85% H₃PO₄ in water (0 ppm) as an external standard. Multiplicity of signals in ¹³C NMR spectra was determined by DEPT, HMQC, CH-cosy, HMBC, and long-range CH-cosy techniques. High-resolution FAB-mass spectral data were obtained on a JEOL JMS-700 spectrometer. Gel permeation liquid chromatography (GPC) was performed on an LC-918 (Japan Analytical Industry Co.,Ltd) equipped with JAIGEL 1H and 2H columns (eluent: toluene). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. All melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Maleic anhydride, *N*-phenylmaleimide, fumaronitrile, and anthracene were recrystallized from benzene, cyclohexane, benzene/hexane, and toluene, respectively. 2,3-Dimethyl-1,3-butadiene and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were distilled from sodium borohydride and sodium hydroxide prior to use, respectively. 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenylphosphine (BbtPH₂),^{S2} 9-Anthryldichlorophosphine,^{S3} maleonitrile,^{S4} and BbtP=PBbt^{S5} were prepared according to the reported procedures.

Synthesis of 9-anthryldiphosphene **1b [BbtP=P(9-Anth)]:** In a glovebox filled with an argon, DBU (93 μ L, 0.62 mmol) was added to a toluene (10 mL) solution of BbtPH₂ (165 mg, 0.251 mmol) and 9-anthryldichlorophosphine (83.7 mg, 0.300 mmol) at room temperature. After stirring at room temperature for 2 h, the reaction mixture was filtered through Celite[®] with toluene. The solvent of the filtrate was removed under reduced pressure, and then the residue was washed with cooled hexane to afford 9-anthryldiphosphene **1b** (167 mg, 0.193 mmol, 77%) as red crystals. **1b**: mp: 229 °C (decomp.). ¹H NMR (400 MHz, C₆D₆, r.t.) δ = 0.31 (s, 36H), 0.43 (s, 27H), 2.87 (s, 2H), 7.19 (s, 2H), 7.28 (ddd, ³J_{HH} = 8.5, 6.5 Hz, ⁴J_{HH} = 1.0 Hz, 2H), 7.46 (ddd, ³J_{HH} = 8.7, 6.5 Hz, ⁴J_{HH} = 1.4 Hz, 2H), 7.80 (d, ³J_{HH} = 8.5 Hz), 8.18 (s, 1H), 8.62 (d, ³J_{HH} = 8.7 Hz, 2H); ¹³C {¹H} NMR (100 MHz, C₆D₆, r.t.) δ = 1.78 (CH₃), 5.60 (CH₃), 22.49, 33.59 (CH), 125.38 (CH), 125.44 (CH), 127.38 (CH), 128.72 (d, ³J_{CP} = 7.4 Hz, CH), 129.61 (CH), 129.79 (CH), 132.26, 133.54 (d, ²J_{CP} = 4.9 Hz), 137.38 (br d, ¹J_{CP} = 44.5 Hz), 139.70 (br d, ¹J_{CP} = 58.6 Hz), 145.64, 146.85; ³¹P NMR (121 MHz, C₆D₆, r.t.) δ = 521.9, 586.8 (AB quartet, ¹J_{PP} = 584 Hz). HRMS (FAB) *m/z*, found: 863.3900 ([M+H]⁺), calcd for C₄₄H₇₇P₂Si₇ ([M+H]⁺): 863.3885. Anal. Found: C, 61.29; H, 8.94%. Calcd for C₄₄H₇₆P₂Si₇: C, 61.19; H, 8.87%.

Reaction of BbtP=P(9-Anth) **1b with 2,3-dimethyl-1,3-butadiene (Scheme 1):** A C₆D₆ suspension (0.9 mL) of BbtP=P(9-Anth) (**1b**, 51.8 mg, 60.0 μ mol) and 2,3-dimethyl-1,3-butadiene (68 μ L, 49 mg, 0.60 mmol) was degassed and sealed in an NMR tube. After heating for 15 h at 60 °C, the solvent was removed under reduced pressure. The residue was separated by GLPC to afford 1,2-diphosphacyclohex-4-ene derivative **2** (37.9 mg, 40.1 μ mol, 67%) as yellow solids. **2**: mp: 198 °C (decomp.). ¹H NMR (400 MHz, C₆D₁₂, 50 °C) δ = -0.33 (br s, 18H), 0.15 (s, 18H), 0.23 (s, 27H), 1.65 (d, *J* = 2.9 Hz, 3H), 2.10 (s, 3H), 2.40 (dt, *J* = 12.6, 10.2 Hz, 1H), 2.51 (dd, *J* = 15.4, 2.8 Hz, 1H), 3.19-3.31 (m, 1H), 3.36 (br s, 2H), 3.41-3.45 (m, 1H), 6.71 (s, 2H), 7.26-7.35 (m, 4H), 7.82 (d, ³J_{HH} = 8.5 Hz, 2H), 8.29 (s, 1H), 9.39 (d, ³J_{HH} = 8.0 Hz, 2H); ¹³C {¹H} NMR (100 MHz, C₆D₁₂, 50 °C) δ = 1.83 (CH₃), 2.24 (CH₃), 5.93 (CH₃), 20.03 (CH₃), 21.40 (CH₃), 22.95, 29.76 (d, ³J_{CP} = 9.1 Hz, CH), 29.96 (d, ³J_{CP} = 9.1 Hz, CH), 31.74 (dd,

$^1J_{CP} = 22.3$ Hz, $^2J_{CP} = 9.1$ Hz, CH₂), 33.24 (dd, $^1J_{CP} = 20.6$ Hz, $^2J_{CP} = 4.9$ Hz, CH₂), 125.12 (CH), 125.48 (CH), 127.80 (dd, $^2J_{CP} = 4.5$ Hz, $^3J_{CP} = 2.1$ Hz), 128.14 (CH), 128.57 (d, $^1J_{CP} = 21.0$ Hz, $^2J_{CP} = 2.9$ Hz), 129.51 (CH), 130.43 (dd, $^3J_{CP} = 20.2$ Hz, $^4J_{CP} = 14.4$ Hz, CH), 130.81 (d, $^2J_{CP} = 4.9$ Hz), 131.24 (CH), 132.86 (dd, $^3J_{CP} = 2.0$ Hz, $^4J_{CP} = 2.0$ Hz), 133.03 (d, $^1J_{CP} = 28.0$ Hz), 138.03 (dd, $^2J_{CP} = 9.5$ Hz, $^3J_{CP} = 4.5$ Hz), 146.75, 153.52; ^{31}P NMR (121 MHz, C₆D₆, r.t.) $\delta = -58.2, -57.4$ (AB quartet, $^1J_{PP} = 208$ Hz). HRMS (FAB) m/z , found: 945.4689 ([M+H]⁺), calcd for C₅₀H₈₇P₂Si₇ ([M+H]⁺): 945.4668. Anal. Found: C, 63.38; H, 9.38%. Calcd for C₅₀H₈₆P₂Si₇: C, 63.50; H, 9.17%.

Reaction of BbtP=P(9-Anth) 1b with maleic anhydride (3a) (Scheme 1): A C₆D₆ suspension (0.9 mL) of BbtP=P(9-Anth) (**1b**, 51.8 mg, 60.0 μmol) and maleic anhydride (**3a**, 17.8 mg, 0.182 mmol) was degassed and sealed in an NMR tube. After heating for 14 h at 120 °C, the reaction mixture was filtered through Celite[®] with toluene. The solvent of the filtrate was removed under reduced pressure, and the residue was separated by GPLC to afford maleic anhydride adduct **4a** (49.1 mg, 51.1 μmol , 85%) as orange crystals. **4a**: mp: 235 °C (decomp.). ^1H NMR (400 MHz, C₆D₆, r.t.) $\delta = 0.368$ (s, 18H), 0.370 (s, 18H), 0.45 (s, 27H), 2.76 (dd, $^3J_{HH} = 9.1$ Hz, 3.3 Hz, 1H), 2.85 (s, 2H), 4.53 (d, $^3J_{HH} = 3.3$ Hz, 1H), 4.55 (br d, $^3J_{HH} = 9.1$ Hz, 1H), 6.77 (ddd, $^3J_{HH} = 7.5$ Hz, 7.3 Hz, $^4J_{HH} = 1.2$ Hz, 1H), 6.84 (ddd, $^3J_{HH} = 7.5$ Hz, 7.3 Hz, $^4J_{HH} = 1.5$ Hz, 1H), 6.92 (ddd, $^3J_{HH} = 7.3$ Hz, 7.3 Hz, $^4J_{HH} = 1.0$ Hz, 1H), 6.97 (dd, $^3J_{HH} = 7.3$ Hz, $^5J_{HH} = 1.5$ Hz, 1H), 7.06 (dd, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.2$ Hz, 1H), 7.14 (ddd, 1H, $^3J_{HH} = 7.8$ Hz, 7.3 Hz, $^4J_{HH} = 1.5$ Hz), ^{S6} 7.26 (s, 2H), 7.74 (d, $^3J_{HH} = 7.8$ Hz, 1H), 7.84 (d, $^3J_{HH} = 7.3$ Hz, 1H); ^{13}C { ^1H } NMR (100 MHz, C₆D₆, r.t.) $\delta = 1.83$ (CH₃), 1.88 (CH₃), 5.67 (CH₃), 22.61, 33.53 (CH), 46.55 (CH), 49.94 (CH), 52.85 (d, $^2J_{CP} = 15.7$ Hz, CH), 56.78 (d, $^1J_{CP} = 66.8$ Hz), 124.60 (CH), 125.60 (d, $^3J_{CP} = 23.9$ Hz, CH), 125.90 (CH), 126.28 (CH), 127.00 (CH), 127.32 (CH), 127.68 (CH \times 2), 127.86 (CH), 134.85 (br d, $^1J_{CP} = 34.6$ Hz), 138.85, 141.13 (br d, $^2J_{CP} = 10.7$ Hz), 142.58, 143.98, 146.39, 147.36, 169.79; ^{31}P NMR (121 MHz, C₆D₆, r.t.) $\delta = 520.3, 571.2$ (AB quartet, $^1J_{PP} = 583$ Hz). HRMS (FAB) m/z ,

found: 961.3905 ($[M+H]^+$), calcd for $C_{48}H_{79}O_3P_2Si_7$ ($[M+H]^+$): 961.3889. Anal. Found: C, 59.67; H, 8.42%. Calcd for $C_{48}H_{78}O_3P_2Si_7$: C, 59.95; H, 8.18%.

Reaction of BbtP=P(9-Anth) 1b with *N*-phenylmaleimide (3b) (Scheme 1): A C_6D_6 suspension (0.9 mL) of BbtP=P(9-Anth) (**1b**, 51.8 mg, 60.0 μ mol) and *N*-phenylmaleimide (**3b**, 31.2 mg, 0.180 mmol) was degassed and sealed in an NMR tube. After heating for 6 h at 120 °C, the reaction mixture was filtered through Celite[®] with toluene. The solvent of the filtrate was removed under reduced pressure, and then the residue was separated by GPLC to afford *N*-phenylmaleimide adduct **4b** (53.7 mg, 51.7 μ mol, 86%) as orange crystals. **4b**: mp: 232 °C (decomp.). 1H NMR (400 MHz, C_6D_6 , r.t.) δ = 0.348 (s, 18H), 0.356 (s, 18H), 0.45 (s, 27H), 2.976 (dd, $^3J_{HH} = 8.5$ Hz, 3.1 Hz, 1H), 2.982 (s, 2H), 4.60 (br d, $^3J_{HH} = 8.5$ Hz, 1H), 4.79 (d, $^3J_{HH} = 3.1$ Hz, 1H), 6.71-6.74 (m, 2H), 6.81-6.91 (m, 3H), 6.96-7.03 (m, 3H), 7.14 (d, $^3J_{HH} = 7.5$ Hz, 1H),^{S6} 7.16 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.4$ Hz, 1H),^{S6} 7.23 (ddd, $^3J_{HH} = 7.5$ Hz, 7.5 Hz, $^4J_{HH} = 1.3$ Hz, 1H), 7.25 (s, 2H), 7.92 (d, $^3J_{HH} = 7.5$ Hz, 1H), 7.94 (d, $^3J_{HH} = 7.5$ Hz, 1H); ^{13}C { 1H } NMR (100 MHz, C_6D_6 , r.t.) δ = 1.83 (CH₃), 1.88 (CH₃), 5.68 (CH₃), 22.52, 33.18 (CH), 47.21 (CH), 49.36 (CH), 52.57 (d, $^2J_{CP} = 13.2$ Hz, CH), 57.05 (d, $^1J_{CP} = 64.3$ Hz), 124.68 (CH), 125.72 (d, $^3J_{CP} = 19.0$ Hz, CH), 125.81 (CH), 126.10 (CH), 126.51 (CH), 127.06 (CH), 127.19 (CH \times 2), 127.26 (br, CH), 127.62 (CH), 128.27 (CH), 128.57 (CH), 132.29, 135.74 (d, $^1J_{CP} = 27.2$ Hz), 139.84, 141.58 (d, $^3J_{CP} = 4.9$ Hz), 143.39, 144.53, 146.42, 146.91, 174.55, 174.61; ^{31}P NMR (121 MHz, C_6D_6 , r.t.) δ = 525.8, 564.3 (AB quartet, $^1J_{PP} = 577$ Hz). HRMS (FAB) m/z , found: 1036.4352 ($[M+H]^+$), calcd for $C_{54}H_{84}NO_2P_2Si_7$ ($[M+H]^+$): 1036.4362. Anal. Found: C, 62.63; H, 8.09; N, 1.40%. Calcd for $C_{54}H_{83}NO_2P_2Si_7$: C, 62.56; H, 8.07; N, 1.35%.

Reaction of BbtP=P(9-Anth) 1b with 5 equiv of fumaronitrile (3c) (Table 1, entry 1): A C_6D_6 suspension (0.9 mL) of BbtP=P(9-Anth) (**1b**, 51.8 mg, 60.0 μ mol) and fumaronitrile (**3c**, 23.4 mg, 0.300

mmol) was degassed and sealed in an NMR tube. After heating for 72 h at 120 °C, the starting material **1b**, fumaronitrile adduct **4c**, and maleonitrile adduct **4d** were observed in the ratio of 14:63:23 as judged by the ¹H NMR spectra together with maleonitrile (**3d**).^{S7} The reaction mixture was separated by GPLC and then PTLC (eluent: benzene, *R_f* = 0.5 for **4c** and 0.4 for **4d**, respectively) to afford fumaronitrile adduct **4c** (25.1 mg, 26.6 μmol, 44%) and maleonitrile adduct **4d** (8.4 mg, 8.9 μmol, 15%) as orange crystals, respectively. **4c**: mp: 210 °C (decomp.). ¹H NMR (400 MHz, C₆D₆, r.t.) δ = 0.29 (s, 18H), 0.35 (s, 18H), 0.42 (s, 27H), 2.59 (s, 2H), 2.67 (dd, ³*J*_{HH} = 4.1 Hz, 2.7 Hz, 1H), 3.92 (d, ³*J*_{HH} = 2.7 Hz, 1H), 4.46 (d, ³*J*_{HH} = 4.1 Hz, 1H), 6.89-7.02 (m, 4H), 7.10-7.16 (m, 2H), 7.20 (s, 2H), 7.65 (d, ³*J*_{HH} = 7.5 Hz, 1H), 7.89 (d, ³*J*_{HH} = 7.5 Hz, 1H); ¹³C {¹H} NMR (100 MHz, C₆D₆, r.t.) δ = 1.84 (CH₃), 1.89 (CH₃), 5.63 (CH₃), 22.65, 34.11 (CH), 38.13 (CH), 42.48 (d, ²*J*_{CP} = 26.4 Hz, CH), 46.94 (CH), 56.68 (d, ¹*J*_{CP} = 63.5 Hz), 118.29, 118.98, 125.19 (CH), 126.19 (br, CH), 126.24 (CH), 126.43 (br d, ³*J*_{CP} = 26.4 Hz, CH), 127.06 (CH), 127.67 (CH), 127.71 (CH×2), 128.20 (CH), 133.74 (d, ¹*J*_{CP} = 30.5 Hz), 139.65, 140.17, 140.42 (d, ²*J*_{CP} = 9.1 Hz), 142.62, 146.40, 147.79; ³¹P NMR (121 MHz, C₆D₆, r.t.) δ = 518.8, 579.4 (AB quartet, ¹*J*_{PP} = 592 Hz); HRMS (FAB) *m/z*, found: 941.4102 ([M+H]⁺), calcd for C₄₈H₇₉N₂P₂Si₇ ([M+H]⁺): 941.4103. Anal. Found: C, 61.07; H, 8.36; N, 3.07%. Calcd for C₄₈H₇₈N₂P₂Si₇: C, 61.22; H, 8.35; N, 2.97%. **4d**: mp: 215 °C (decomp.). ¹H NMR (400 MHz, C₆D₆, r.t.) δ = 0.35 (s, 18H), 0.37 (s, 18H), 0.44 (s, 27H), 2.29 (dd, ³*J*_{HH} = 9.7 Hz, 2.2 Hz, 1H), 2.65 (s, 2H), 3.98 (d, ³*J*_{HH} = 2.2 Hz, 1H), 4.11 (d, ³*J*_{HH} = 9.7 Hz, 1H), 6.83 (dd, ³*J*_{HH} = 7.3 Hz, ⁴*J*_{HH} = 1.2 Hz, 1H), 6.88-6.93 (m, 2H), 6.96 (ddd, ³*J*_{HH} = 7.5 Hz, 7.3 Hz, ⁴*J*_{HH} = 1.5 Hz, 1H), 7.08 (ddd, ³*J*_{HH} = 7.8 Hz, 7.5 Hz, ⁴*J*_{HH} = 1.2 Hz, 1H), 7.18 (dd, ³*J*_{HH} = 7.0 Hz, ⁴*J*_{HH} = 1.5 Hz, 1H), 7.23 (s, 2H), 7.57 (d, ³*J*_{HH} = 7.8 Hz, 1H), 7.86 (d, ³*J*_{HH} = 7.3 Hz, 1H); ¹³C {¹H} NMR (100 MHz, C₆D₆, r.t.) δ = 1.83 (CH₃), 1.90 (CH₃), 5.66 (CH₃), 22.71, 34.06 (CH), 36.64 (CH), 41.02 (CH, d, ²*J*_{CP} = 26.4 Hz), 47.18 (CH), 56.70 (d, ¹*J*_{CP} = 61.0 Hz), 117.31, 117.73, 124.65 (CH), 126.14 (br d, ³*J*_{CP} = 23.9 Hz, CH), 126.37 (CH), 126.43 (br, CH), 126.68 (CH), 127.70 (CH), 127.78 (CH), 127.82 (CH), 128.07 (CH), 133.80 (d, ¹*J*_{CP} = 33.0 Hz), 138.61, 140.59 (d, ²*J*_{CP} = 4.9 Hz), 141.53, 142.67, 146.36, 147.84; ³¹P NMR (121 MHz, C₆D₆, r.t.) δ = 522.6, 578.3 (AB quartet, ¹*J*_{PP} =

592 Hz). HRMS (FAB) m/z , found: 941.4092 ($[M+H]^+$), calcd for $C_{48}H_{79}N_2P_2Si_7$ ($[M+H]^+$): 941.4103. Anal. Found: C, 61.11; H, 8.37; N, 3.06%. Calcd for $C_{48}H_{78}N_2P_2Si_7$: C, 61.22; H, 8.35; N, 2.97%.

Reaction of BbtP=P(9-Anth) 1b with 30 equiv of fumaronitrile (3c) (Table 1, entry 2): A C_6D_6 suspension (0.9 mL) of BbtP=P(9-Anth) (**1b**, 51.8 mg, 60.0 μ mol) and fumaronitrile (**3c**, 141 mg, 1.81 mmol) was degassed and sealed in an NMR tube. After heating for 13 h at 120 °C, the starting material **1b** and fumaronitrile adduct **4c** were observed in the ratio of 3:97 as judged by the 1H NMR spectra together with maleonitrile (**3d**).^{S7} After the reaction mixture was filtered through Celite[®] with toluene, the solvent of the filtrate was removed under reduced pressure. The residue was separated by GLPC and then PTLC (benzene as eluent) to afford fumaronitrile adduct **4c** (47.1 mg, 50.0 μ mol, 83%) as orange crystals.

Reaction of BbtP=P(9-Anth) 1b with 30 equiv of maleonitrile (3d) (Table 1, entry 3): A C_6D_6 suspension (0.9 mL) of BbtP=P(9-Anth) (**1b**, 51.8 mg, 60.0 μ mol) and maleonitrile (**3d**, 141 mg 1.81 mmol) was degassed and sealed in an NMR tube. After heating for 12 h at 120 °C, the starting material **1b** and maleonitrile adduct **4d** were observed in the ratio of 3:97 as judged by the 1H NMR spectra together with trace amount of **4c** and fumaronitrile (**3c**).^{S7} The reaction mixture was separated by GLPC and then PTLC (benzene as eluent) to afford maleonitrile adduct **4d** (40.2 mg, 42.7 μ mol, 71%) as orange crystals.

Reaction of anthracene with 5 equiv of fumaronitrile (3c): A C_6D_6 suspension (0.9 mL) of anthracene (10.7 mg, 60.0 μ mol) and fumaronitrile (**3c**, 23.4 mg, 0.300 mmol) was degassed and sealed in an NMR tube. After heating for 24 h at 120 °C, the signals of anthracene disappeared as judged by

the ^1H NMR spectra. No change was observed by ^1H NMR spectra after the additional heating for 48 h at 120 °C. The unreacted fumaronitrile and the solvent of the reaction mixture were removed under reduced pressure to afford the [4+2] cycloadduct **5c** (15.6 mg, 60 μmol , >99%) as colorless solids. **5c**: mp: 194 °C (sublimed; lit.^{S8} 274 °C, lit.^{S9} 259 °C, lit.^{S10} 259-260 °C). ^1H NMR (400 MHz, CDCl_3 , r.t.) δ = 3.13-3.14 (m, 2H), 4.64 (m, 2H), 7.23-7.30 (m, 4H), 7.34-7.38 (m, 2H), 7.44-7.47 (m, 2H); ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , r.t.) δ = 35.47 (CH), 46.32 (CH), 118.47, 124.16 (CH), 125.75 (CH), 127.82 (CH), 127.91 (CH), 137.33, 139.27. HRMS (EI) m/z , found: 256.0996 ($[\text{M}]^+$), calcd for $\text{C}_{18}\text{H}_{12}\text{N}_2$ ($[\text{M}]^+$): 256.1000. Anal. Found: C, 84.43; H, 4.84; N, 10.83%. Calcd for $\text{C}_{18}\text{H}_{12}\text{N}_2$: C, 84.35; H, 4.72; N, 10.93.

Reaction of anthracene with 5 equiv of maleonitrile (3d): A C_6D_6 suspension (0.9 mL) of anthracene (10.7 mg, 60.0 μmol) and maleonitrile (**3d**, 23.4 mg, 0.300 mmol) was degassed and sealed in an NMR tube. After heating for 24 h at 120 °C, the signals of anthracene disappeared as judged by the ^1H NMR spectra. No change was observed by ^1H NMR spectra after the additional heating for 48 h at 120 °C. The supernatant of the reaction mixture was removed, and then the residue was washed with benzene to afford the [4+2] cycloadduct **5d** (15.0 mg, 58.5 μmol , 97%) as colorless solids. **5d**: mp: 225 °C (sublimed; lit.^{S10} 269-270 °C). ^1H NMR (400 MHz, CDCl_3 , r.t.) δ = 3.33-3.34 (m, 2H), 4.67 (m, 2H), 7.22 (dd, $J_{\text{HH}} = 5.5, 3.1$ Hz, 2H), 7.32 (dd, $J_{\text{HH}} = 5.5, 3.3$ Hz, 2H), 7.35 (dd, $J_{\text{HH}} = 5.5, 3.3$ Hz, 2H), 7.49 (dd, $J_{\text{HH}} = 5.5, 3.1$ Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , r.t.) δ = 34.50 (CH), 46.55 (CH), 117.21, 124.37 (CH), 125.66 (CH), 127.73 (CH), 128.03 (CH), 137.63, 139.32. HRMS (EI) m/z , found: 256.0996 ($[\text{M}]^+$), calcd for $\text{C}_{18}\text{H}_{12}\text{N}_2$ ($[\text{M}]^+$): 256.1000. Anal. Found: C, 84.11; H, 4.83; N, 11.51%. Calcd for $\text{C}_{18}\text{H}_{12}\text{N}_2$: C, 84.35; H, 4.72; N, 10.93.

Thermal Reaction of fumaronitrile (3c): A C₆D₆ solution (0.75 mL) of fumaronitrile (**3c**, 15.6 mg, 0.20 mmol) was degassed and sealed in an NMR tube. After heating for 60 h at 120 °C, no change was observed by ¹H NMR spectrum.

Isomerization of fumaronitrile (3c) into maleonitrile (3d) in the presence of diphosphene (BbtP=PBbt): A C₆D₆ solution (0.6 mL) of BbtP=PBbt (6.6 mg, 5.0 μmol) and fumaronitrile (**3c**, 11.7 mg, 0.150 mmol) was degassed and sealed in an NMR tube. After heating for 24 h at 120 °C, fumaronitrile (**3c**) and maleonitrile (**3d**) were observed in the ratio of 68:32 as judged by ¹H NMR spectrum.

Isomerization of maleonitrile (3d) into fumaronitrile (3c) in the presence of diphosphene (BbtP=PBbt): A C₆D₆ solution (0.6 mL) of BbtP=PBbt (6.6 mg, 5.0 μmol) and maleonitrile (**3d**, 12.6 mg, 0.161 mmol) was degassed and sealed in an NMR tube. After heating for 24 h at 120 °C, fumaronitrile (**3c**) and maleonitrile (**3d**) were observed in the ratio of 14:86 as judged by ¹H NMR spectrum.

Thermal reactions of the maleimide adduct 4b in the presence of 20 equiv of maleic anhydride (3a): A C₆D₆ solution (0.7 mL) of maleimide adduct **4b** (7.4 mg, 7.1 μmol) and maleic anhydride (**3a**, 14.4 mg, 0.147 mmol) as a trapping reagent for anthryldiphosphene **1b** was degassed and sealed in an NMR tube. After heating for 48 h at 120 °C, no change was observed by ¹H NMR spectrum.

Thermal reactions of [4+2] cycloadducts 4a, 4c, and 4d in the presence of *N*-phenylmaleimide: A C₆D₆ solution (0.7 mL) of [4+2] cycloadduct **4** (7.2 μmol) and *N*-phenylmaleimide (**3b**, 12.5 mg, 72.2 μmol) was degassed and sealed in an NMR tube, and then heated for 24 h at 120 °C.

With maleic anhydride adduct **4a** (6.9 mg), the signals for **4a**, maleimide adduct **4b** generated from the [4+2] cycloaddition of anthryldiphosphene **1b** and **3b**, and the dissociated olefin **3a** was observed in the ratio of 88/12/4 (**4a/4b/3a**).

With fumaronitrile adduct **4c** (6.8 mg), the signals for **4c**, maleimide adduct **4b**, and the dissociated olefin **3c** was observed in the ratio of 83/17/4 (**4c/4b/3c**).

With maleonitrile adduct **4d** (6.8 mg), the signals for **4d**, maleimide adduct **4b**, and the dissociated olefin **3d** was observed in the ratio of 63/37/18 (**4d/4b/3d**).

X-Ray crystallographic analysis of 1b and 4a-d: The intensity data were collected with a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71070$ Å) (for **1b**, **4a**, **4b**, and **4d**) or a Rigaku Saturn70 CCD system with VariMax Mo Optic using Mo K_{α} radiation ($\lambda = 0.71070$ Å) (for **4c**) at a temperature of 103(2) K. The structures were solved by direct methods (SIR-97^{S11} or SHELXS-97^{S12}) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).^{S13} All hydrogen atoms were placed using AFIX instructions, while all the other atoms were refined anisotropically. Additional crystal data and detail of the data collection and structure refinement are given in Table S1 and S2, and the molecular structures of [**4b**·3benzene], **4c**, and [**4d**·1.5benzene] with thermal ellipsoid plot (50% probability) were shown in Figure S1-S3, respectively.

Table S1: Crystal Data for Compounds **1b**, [**4a**·1.5benzene], and [**4b**·3benzene].

	1b	[4a ·1.5benzene]	[4b ·3benzene]
formula	C ₄₄ H ₇₆ P ₂ Si ₇	C ₅₇ H ₈₇ O ₃ P ₂ Si ₇	C ₇₂ H ₁₀₁ NO ₂ P ₂ Si ₇
<i>M</i> _w	863.62	1078.84	1271.11
crystal dimension (mm ⁻³)	0.30 × 0.10 × 0.10	0.25 × 0.20 × 0.10	0.45 × 0.30 × 0.20
crystal system	triclinic	triclinic	tetragonal
space group	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)	<i>I</i> -4 (#82)
<i>a</i> (Å)	12.3313(5)	11.7476(3)	34.142(12)
<i>b</i> (Å)	12.2910(4)	12.6699(3)	34.142(12)
<i>c</i> (Å)	19.5641(9)	22.2004(7)	12.635(4)
<i>α</i> (°)	72.6570(19)	74.0631(12)	90
<i>β</i> (°)	82.893(2)	79.3447(14)	90
<i>γ</i> (°)	63.6039(18)	88.6068(15)	90
<i>V</i> (Å ³)	2535.18(18)	3121.32(15)	14728(9)
<i>Z</i>	2	2	8
<i>ρ</i> _{calcd} (g cm ⁻³)	1.131	1.148	1.146
<i>μ</i> (mm ⁻¹)	0.280	0.243	0.215
2 θ _{max} (°)	51	51	51
no. of reflections	17954	22309	62150
no. of independent reflections	9182	11366	13673
no. of parameters	499	643	778
R _{int}	0.0620	0.0639	0.0606
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0511	0.0520	0.0843
<i>wR</i> ₂ (all data)	0.0893	0.0957	0.2332
Residual electron density (eÅ ⁻³)	-0.317 and 0.314	-0.476 and 0.703	-0.478 and 0.813
GOF	1.010	1.036	1.074

Table S2: Crystal Data for Compounds **4c**, and [**4d**·1.5benzene].

	4c	[4d ·1.5benzene]
formula	C ₄₈ H ₇₈ N ₂ P ₂ Si ₇	C ₅₇ H ₈₇ N ₂ P ₂ Si ₇
<i>M</i> _w	941.69	1058.86
crystal dimension (mm ⁻³)	0.20 × 0.02 × 0.01	0.20 × 0.20 × 0.10
crystal system	triclinic	triclinic
space group	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)
<i>a</i> (Å)	9.0157(4)	11.804(5)
<i>b</i> (Å)	14.2460(7)	12.676(6)
<i>c</i> (Å)	23.6907(12)	22.115(9)
<i>α</i> (°)	73.902(2)	74.025(11)
<i>β</i> (°)	82.098(3)	79.207(11)
<i>γ</i> (°)	71.202(4)	88.701(11)
<i>V</i> (Å ³)	2763.6(2)	3123(2)
<i>Z</i>	2	2
<i>ρ</i> _{calcd} (g cm ⁻³)	1.132	1.126
<i>μ</i> (mm ⁻¹)	0.263	0.239
2 θ _{max} (°)	51	51
no. of reflections	24412	27384
no. of independent reflections	10218	11509
no. of parameters	553	634
R _{int}	0.1072	0.0858
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0628	0.0747
wR ₂ (all data)	0.1285	0.1502
Residual electron density (eÅ ⁻³)	-0.335 and 0.372	-0.502 and 0.660
GOF	1.015	1.113

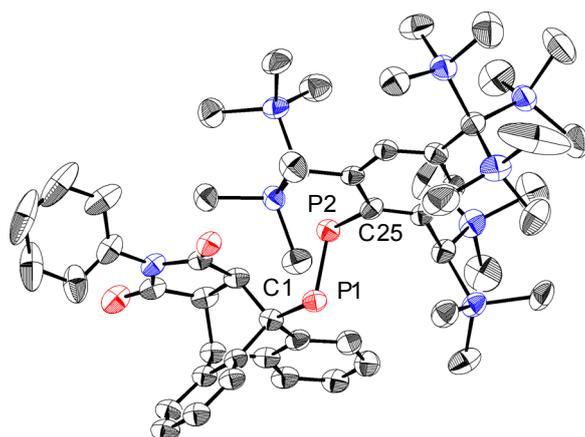


Figure S1. Molecular structure of [4b·3benzene] with thermal ellipsoid plot (50% probability). All hydrogen atoms and solvent molecules (benzene) are omitted for clarity. Selected bond length [Å] and angles [deg]: P(1)–P(2) 2.022(2), P(1)–C(1) 1.889(6), P(2)–C(25) 1.834(6), C(1)–P(1)–P(2) 101.58(18), C(25)–P(2)–P(1) 105.43(19).

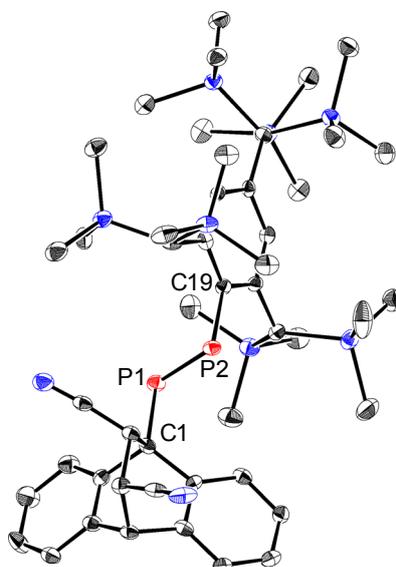


Figure S2. Molecular structure of 4c with thermal ellipsoid plot (50% probability). All hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [deg]: P(1)–P(2) 2.0366(14), P(1)–C(1) 1.903(4), P(2)–C(19) 1.839(4), C(1)–P(1)–P(2) 100.34(12), C(19)–P(2)–P(1) 103.25(12).

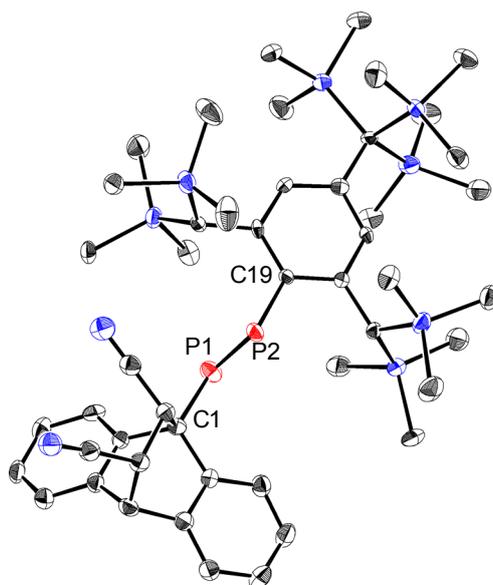


Figure S3. Molecular structure of [4d·1.5benzene] with thermal ellipsoid plot (50% probability). All hydrogen atoms and solvent molecules (benzene) are omitted for clarity. Selected bond length [Å] and angles [deg]: P(1)–P(2) 2.0383(18), P(1)–C(1) 1.896(4), P(2)–C(19) 1.845(4), C(1)–P(1)–P(2) 103.17(15), C(19)–P(2)–P(1) 103.80(14).

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