Radialene Chemistry

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Synthesis and Properties of 4,5,6-Triphospha[3]radialene[**]

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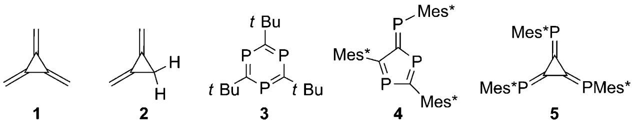
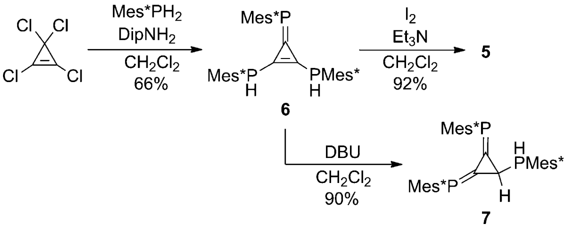
Radialenes are a unique class of unsaturated hydrocarbons and have attracted much attention from the viewpoint of their cross- conjugated π-electron electronic structures.[1] For example, [3]radialene (**1**, Scheme 1),[2] the smallest radialene, exhibits rather strong UV absorption at longer wavelengths than dimethylenecyclopropane (**2**),[1b] which reflects the extension of the π-conjugated system. Compound **1** is an important research target because the difference in properties between **1** and its structural isomer, benzene, is a fundamental issue of π-electron conjugation and π-electron cross-conjugation. A number of [3]radialene derivatives that contain extended π-conjugated systems have been synthesized and their unique optical and electrochemical properties were reported.[3]



Scheme 1. Structures of related and isomeric compounds of 4,5,6-triphospha[3]radialene.

On the other hand, there has been much interest in the chemistry of compounds that contain P=C bonds, because π-bonds that contain a heavier main-group element, such as phosphorus, are known to have unique electronic characteristics.[4] Although compounds that contain a double bond to a heavier main-group element are known to be highly reactive and difficult to isolate as a stable compound, during the past three decades a number of phosphaalkenes that contain a P=C bond have been synthesized as stable compounds by taking advantage of kinetic stabilization.[4] As a result, it was found that P=C bonds have unique characteristics that are different from those of C=C bonds, for example, they have lower LUMO levels relative to compounds with N=N or C=C double bonds. These unique characteristics of radialenes and low-coordinated phosphorus compounds prompted us to research the chemistry of the phosphorus analogues of radialenes, which are an attractive research target as a result of the synergy between the unique nature of radialenes and P=C bonds. Especially, we became interested in the chemistry of 4,5,6-tris(2,4,6-tri-*tert*-butylphenyl)triphospha[3]radialene, as its skeletal isomers 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**3**)[5] and 1,3,6-tris(2,4,6-tri-*tert*-butylphenyl)triphosphafulvene (**4**)[6] have already been synthesized as stable compounds. However, studies of heteroatom-containing [3]radialene derivatives have been quite limited because of their instability,[4b,7] whereas some [4] or [6]radialene derivatives that contain nitrogen,[8] oxygen,[9] phosphorus,[10] or sulfur atoms[9b] in the framework have been isolated, and their characteristic properties that are derived from their carbon–heteroatom π-bond demonstrated. Herein, we report the synthesis of a stable triphospha[3]radialene derivative **5**, in which the three *exo*-carbon atoms of the [3]radialene skeleton are replaced by phosphorus atoms.

The reaction of tetrachlorocyclopropene[11] with the bulky (2,4,6-tri-*tert*-butylphenyl)phosphine[12] in the presence of 2,6-diisopropylaniline as a base gave a diastereomeric mixture of 4-phosphatriafulvenes[13] **6** as a stable orange solid in 66% yield (Scheme 2). Oxidation of **6** with iodine in the presence of triethylamine afforded **5** as a deep-purple solid in 92% yield. Compound **5** is a stable phosphorus-containing [3]radialene derivative that contains cross-conjugated P=C bond moieties. It is stable enough to be handled in air without any decomposition. On the other hand, it was found that treatment of **6** with 0.1 equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave a diastereomeric mixture of diphosphinidenecyclopropanes **7** as a yellow solid in 90% yield by a [1,3]-proton shift reaction. Compound **7** is thought to be a good example of a P=C−C=P conjugated π-electron system relative to the cross-conjugated system of **5**.



Scheme 2. Synthesis of **5** and **7**. Mes* = 2,4,6-(tBu)$_3$C$_6$H$_2$; Dip = 2,6-(iPr)$_2$C$_6$H$_3$.

Compounds **5**, **6**, and **7** were fully characterized by NMR spectroscopy, MS, and elemental analysis, and their structures were finally determined by X-ray crystallographic analysis (Figure 1). The lengths of the three P=C bonds of the central

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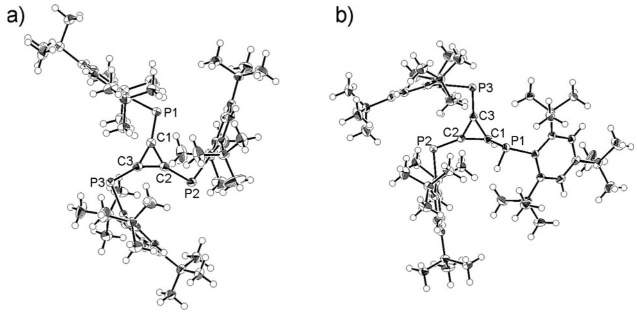


Figure 1. Molecular structures of (a) **5** and (b) **7** with thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: (a) P1–C1 1.6817(14), P2–C2 1.6870(15), P3–C3 1.6870(14), C1–C2 1.436(2), C1–C3 1.438(2), C2–C3 1.432(2); C2-C1-C3 59.76(10), C3-C2-C1 60.19(10), C2-C3-C1 60.05(10); (b) P1–C1 1.8635(17), P2–C2 1.6679(17), P3–C3 1.6737(18), C1–C2 1.507(2), C1–C3 1.507(2), C2–C3 1.406(2); C3-C1-C2 55.67(11), C3-C2-C1 62.07(12), C2-C3-C1 62.26(12).

framework of **5** are almost identical to each other in the range of 1.68–1.69 Å, which is much shorter than the typical length of a P–C bond (1.85–1.90 Å) and slightly longer than that of a nonconjugated P=C bond (for example, (*E*)-Mes*P=CHPh: 1.660(6) Å, (*Z*)-Mes*P=CHPh: 1.674(2) Å).[14] The lengths of C–C bonds in the cyclopropane skeleton (1.43-1.44 Å) of **5** are considerably shorter than that of cyclopropane (1.510(2) Å).[15] These structural features are similar to those of [3]radialene (**1**, C=C: 1.343(20), C–C: 1.453(20) Å).[2b] The bond lengths of the 1,4-diphosphabutadiene moiety of **7** (P2–C2: 1.6679(17) Å; P3–C3: 1.6737(18) Å; C2–C3: 1.406(2) Å) are slightly shorter than those of the exocyclic P=C bonds and the endocyclic C–C bonds of **5**, respectively.

On the basis of the analogy with all-carbon systems, the slight difference in the bond lengths between **5** and **7** is a result of cross-π-conjugation in the triphospha[3]radialene skeleton, that is, the calculated bond lengths of the butadiene moiety of **2** (C=C: 1.312, C–C: 1.421 Å) were also reported to be slightly shorter than those of **1** (C=C: 1.316, C–C: 1.442 Å).[16] Data from ^{31}P NMR, ^{13}C NMR, and ^{1}H NMR spectra suggest that **5** has a C_3 symmetric structure in solution. In the ^{31}P NMR spectrum of **5**, a characteristic signal was detected at $\delta = 187.5$ in C_6D_6. The value is within the range for those of phosphaalkenes, but is slightly shifted to higher field from that of simple phosphaalkene, such as Mes*P=CMe$_2$ ($\delta = 223.0$ in $CDCl_3$)[17] or 1,4-diphosphabutadiene Mes*P=CH–CH=PMes* ($\delta = 243$–285 for three different geometries in $CDCl_3$).[18] In the ^{31}P NMR spectrum of **7**, the signals from the low-coordinate phosphorus atoms were detected in a similar region (δ 192–226 in C_6D_6). The $^{1}J_{PC}$ coupling constant of the P=C bonds in **5** is 54 Hz, the value of which is within the typical range for phosphaalkenes (Mes*P=CPh$_2$: 45.4 Hz,[14] (*E*)-Mes*P=CHPh: 53.1 Hz,[19] (*Z*)-Mes*P=CHPh: 62.9 Hz[15]).

The UV/Vis spectrum of **5** in *n*-hexane has a strong absorption at $\lambda_{max} = 526$ nm ($\varepsilon = 1.92 \times 10^4$, Figure 2), which is at a much longer wavelength than that of [3]radialene (**1**) ($\lambda_{max} = 289$ nm, $\varepsilon = 9390 \pm 1170$)[2c] and reflects the character of a phosphorus-containing π-conjugated system. Moreover, the absorption of **5** was detected at considerably longer wavelengths relative to that of **7** ($\lambda_{max} = 377$ nm, $\varepsilon = 1.35 \times 10^4$), which suggests effective cross-conjugation among the three P=C bonds of **5**. A similar red-shift was detected in the absorption wavelength of dimethylenecyclopropane (**2**, 232 nm) versus [3]radialene (289 nm).[1b] To elucidate the nature of the characteristic absorption of **5**, theoretical calculations for model compound tris(2,6-di-*tert*-butylphenyl)-substituted triphospha[3]radialene derivative **5′** were carried out at the HF/6-31+G(3d)[P]:6-31G(d)[C,H]//B3PW91/6-31+G(3d)[P]:6-31G(d)[C,H] level. The calculated frontier molecular orbitals of **5′** are shown in Figure 3.

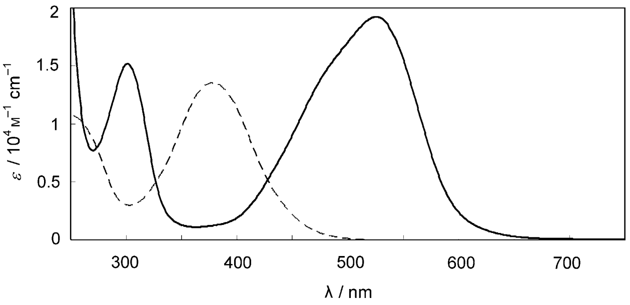


Figure 2. UV/Vis absorption spectra of **5** (solid line) and **7** (dashed line).

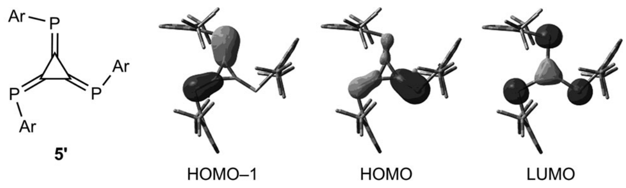
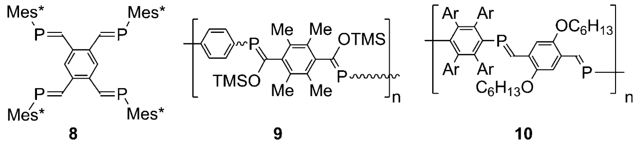


Figure 3. Frontier molecular orbitals of **5′**. Ar = 2,6-(tBu)$_2$C$_6$H$_3$.

The calculated HOMO, HOMO−1, and LUMO of **5′** are composed of the π-conjugated system of the triphospha[3]-radialene framework. The time-dependent DFT (TD-DFT) calculations for **5′** at the B3PW91/6-311+G(3d)[P]:6-31+G(d)[C,H]//B3PW91/6-31+G(3d)[P]:6-31G(d)[C,H] level found two excitation states at $\lambda = 467.8$ ($f = 0.2325$) and $\lambda = 467.7$ nm ($f = 0.2315$) were dominant as a result of the HOMO→LUMO and HOMO−1→LUMO transitions, respectively. The transitions seem to correspond to the absorption of **5** at $\lambda_{max} = 526$ nm. The λ_{max} value of **5** is at a longer wavelength than that of other long π-conjugated systems, such as tetra(phosphaalkenyl)benzene derivative **8** (442 nm, $\varepsilon = 1.92 \times 10^4$)[20] as well as the P=C-bond-containing π-conjugated polymers **9** (323–338 nm)[21] and **10** (445 nm,[22] Scheme 3), even though the π-system of **5** is limited to the C_3P_3 triphospha[3]radialene core.

The cyclic voltammograms of **5** and **7** in THF at room temperature have reversible reduction couples at $E_{1/2} = -1.55$ and -2.10 V (versus ferrocene/ferrocenium$^+$ (FcH/FcH$^+$)), respectively, which shows the higher electron-accepting ability of these two compounds relative to a simple phos-



Scheme 3. π-Conjugated compounds that contain P=C bonds. Ar = 4-(*t*Bu)C$_6$H$_4$.

phaalkene, such as (*E*)-Mes*P=CHPh ($E_{1/2} = -2.54$ V versus FcH/FcH$^+$).[23,24] The much higher reduction potential of **5** relative to **7** shows that the electron-accepting ability is effectively raised by the cross-conjugated system in **5**. On the other hand, the cyclic voltammogtrams of **5** and **7** both have an irreversible oxidation wave at almost the same potential.

Compound **5** can be divided into 1,4-diphosphabutadiene moiety (Fragment A) and phosphaethene moiety (Fragment B, Figure 4). To elucidate the electronic structure of **5**, the molecular orbitals of triphospha[3]radialene **5″**, diphosphinidenecyclopropane **7′**, and phosphinidencyclopropane **11**, the π-conjugated model of **5**, Fragments A, and B, were computed at the HF/6-31G(d,p)//B3PW91/6-31G(d,p) level. The structural properties in the central frameworks of the optimized structures of **5″** and **7′** are in good agreement with those of **5** and **7**, respectively. The molecular orbitals of **5″** can be explained by the interaction between the two conjugated π-electron systems of **7′** and **11**. The interaction between the HOMOs of **7′** and **11** are mismatched in their phase with no effective overlapping. Thus, the HOMO−1 of **5″** (−8.67 eV) is dominantly composed of the HOMO of **7′** (−8.50 eV). The HOMO of **11** (−9.18 eV) can be overlapped with HOMO−3 of **7′** (−10.98 eV) in the same phase, which makes the HOMO of **5″** (−8.67 eV) and is located at higher energy. However, the energy level is still similar to that of HOMO of **7′**. On the other hand, the LUMOs of **7′** (0.04 eV) and **11** (2.19 eV) can make an effective association in the same phase, which makes the LUMO level of **5″** much lower (−1.38 eV). Thus, the LUMO level of **5″** is much lower than that of **7′**, although their HOMO levels are similar to each other. These results support the higher electron-accepting ability of **5** ($E_{1/2} = -1.55$ V vs FcH/FcH$^+$) relative to **7** ($E_{1/2} = -2.10$ V vs FcH/FcH$^+$) on the basis of the cyclic voltammetry.

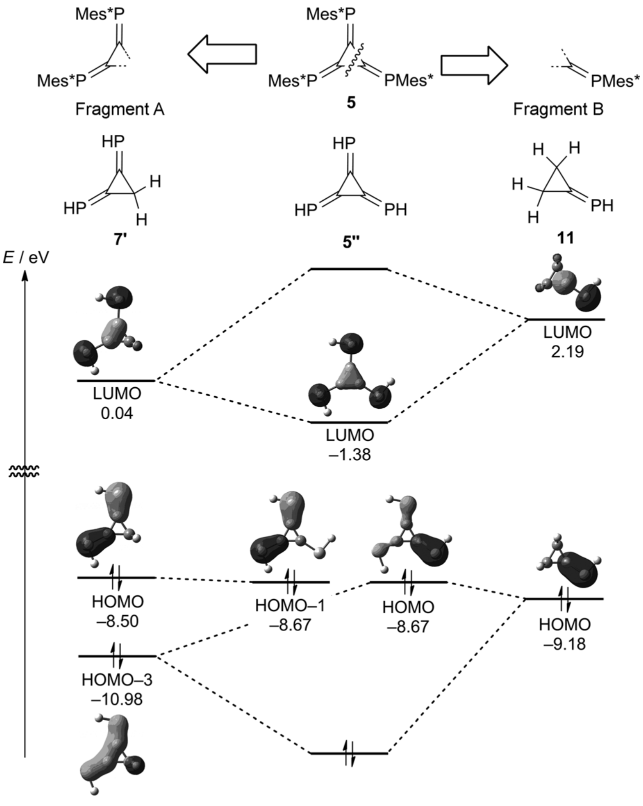


Figure 4. Frontier molecular orbitals of 5′ and 7′and the corresponding energies.

The molecular orbitals of 1,3,5-triphosphabenzene (**3′**), the structural isomer of **5″**, and their carbon analogues, [3]radialene (**1**) and benzene, were also calculated at the same level (Figure 5). The calculated LUMO level of **5″** (−1.38 eV) is much lower than that of **3′** (0.79 eV). In fact, the color of **3** was reported to be pale yellow,[5] which is in sharp contrast to the deep-purple color of **5** and shows that the HOMO–LUMO gap in **5** is smaller than that in **3**. In the case of the all-carbon systems, the LUMO energy of **1** is also lower than that of benzene. Furthermore, the calculated LUMO levels of the phosphorus-containing compounds **5″** and **3′** are much lower than those of the corresponding carbon analogues **1** and benzene. On the other hand, all of the calculated HOMO levels were at similar levels, as shown in Figure 5. Thus, both the [3]radialene framework and the phosphorus substitution should significantly lower the LUMO levels without changing the HOMO level so much. The unique electronic structure of triphospha[3]radialene can be explained by the synergistic effect of both of the factors.[25]

In summary, 4,5,6-triphospha[3]radialene derivative **5** was successfully synthesized by a simple procedure and can be easily handled in the air under ambient conditions, despite the [3]radialene moiety containing P=C bonds. Furthermore, we have revealed that **5** exhibits red-shifted absorption and high electron-accepting ability, which reflects the unique phosphorus-containing cross-conjugated skeleton. These results indicate the potential utility of heteroatom-containing radialenes for molecular electronics.

Experimental Section

Synthesis of **6**: Tetrachlorocyclopropene (0.12 mL, 0.98 mmol) was added to a solution of Mes*PH$_2$ (0.84 g, 3.0 mmol) and 2,6-diisopro-

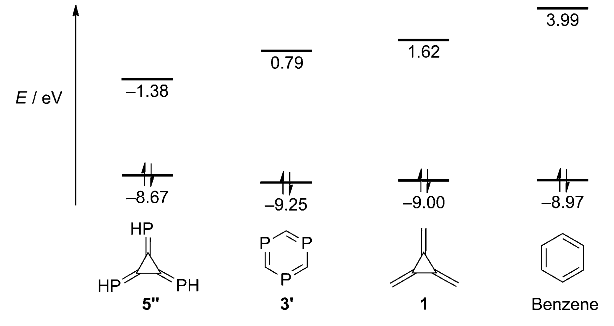


Figure 5. HOMO and LUMO levels of some phosphorus-containing π-conjugated compounds (C$_3$P$_3$H$_3$) and their carbon analogues (C$_6$H$_6$).

pylaniline (0.95 mL, 5.0 mmol) in dichloromethane (5 mL) at room temperature in an argon atmosphere. After the reaction mixture was stirred for 5 h, the solvents were removed under reduced pressure. *n*-Hexane was added to the residue, and then the mixture was filtered through Celite. After removal of the volatile materials, the residue was filtered through a short-path silica gel pad (*n*-hexane). After removal of the solvent, reprecipitation of the residue from dichloromethane/EtOH afforded **6** as a diastereomeric mixture (0.57 g, 0.66 mmol, 66 %). **6**: orange crystals, m.p. 168–170 °C (decomp). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.28$–1.77 (m, 81 H), 5.47 (d, $J_{\mathrm{PH}} = 246$ Hz), 5.75 (d, $J_{\mathrm{PH}} = 244$ Hz), 6.78 (d, $^1J_{\mathrm{PH}} = 342$ Hz), 7.40–7.67 ppm (m, 6 H); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta = 31.5$ (CH_3, s), 31.6 (CH_3, s), 32.1 (CH_3, s), 33.8–34.1 (CH_3, m), 34.9–35.3 (C, m), 37.9–38.7 (C, m), 119.4–119.8 (CH, m), 121.9–122.8 (CH, m), 124.9 (C, d, $J_{\mathrm{PC}} = 23$ Hz), 125.1 (C, d, $J_{\mathrm{PC}} = 21$ Hz), 126.0 (C, d, $J_{\mathrm{PC}} = 26$ Hz), 126.7 (C, d, $J_{\mathrm{PC}} = 25$ Hz), 142.1 (C, d, $J_{\mathrm{PC}} = 59$ Hz), 142.3 (C, d, $J_{\mathrm{PC}} = 59$ Hz), 148.1 (C, s), 151.2 (C, s), 152.0 (C, s), 155.0–157.5 (C, m), 160.9 (C, dd, $J_{\mathrm{PC}} = 53$, 21 Hz), 164.5 ppm (C, dd, $J_{\mathrm{PC}} = 87$, 6 Hz); ^{31}P NMR (120 MHz, C_6D_6) major isomer: $\delta = -74.6$ (d, $J_{\mathrm{PH}} = 246$ Hz), -72.9 (ddd, $J_{\mathrm{PH}} = 246$ Hz, $J_{\mathrm{PP}} = 5$, 7 Hz), 12.5 ppm (d, $J_{\mathrm{PP}} = 5$ Hz); minor isomer: $\delta = -77.0$ (dd, $J_{\mathrm{PH}} = 242$ Hz, $J_{\mathrm{PP}} = 16$ Hz), -76.0 (ddd, $J_{\mathrm{PH}} = 244$ Hz, $J_{\mathrm{PP}} = 16$, 7 Hz), 14.8 ppm (d, $J_{\mathrm{PP}} = 7$ Hz); HRMS (FAB): *m*/*z*: calcd for $C_{57}H_{89}P_3$: 866.6177. Found 866.6116 [M^+]. Elemental analysis calcd (%) for $C_{57}H_{89}P_3$: C 78.94, H 10.34; found: C 78.34, H 10.16.

Synthesis of **5**: Iodine (50 mg, 0.20 mmol) was added to a solution of **6** (87 mg, 0.10 mmol) and triethylamine (70 µL, 0.50 mmol) in dichloromethane (2 mL) at room temperature. After the reaction mixture was stirred for 30 min, the volatile materials were removed under reduced pressure. The residue was extracted with *n*-hexane and aqueous ammonium chloride, and the organic phase was washed with aqueous sodium sulfite. After removal of the solvent, reprecipitation of the residue from dichloromethane/EtOH afforded **5** (80 mg, 92 µmol, 92 %). **5**: purple crystals, m.p. 225 °C (decomp). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.38$ (s, 27 H), 1.54 (s, 54 H), 7.60 ppm (s, 6 H); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): $\delta = 31.6$ (CH_3, s), 33.4 (CH_3, s), 35.0 (C, s), 38.2 (C, s), 122.5 (CH, s), 138.4 (C, dd, $J_{\mathrm{PC}} = 40$, 22 Hz), 150.4 (C, s), 153.9 (C, s), 160.9 ppm (C, ddd, $J_{\mathrm{PC}} = 54$, 32, 11 Hz); ^{31}P NMR (120 MHz, C_6D_6): $\delta = 187.5$ ppm (s); HRMS (FAB): *m*/*z*: calcd for $C_{57}H_{87}P_3$: 864.6021. Found 864.5930 [M^+]. Elemental analysis calcd (%) for $C_{57}H_{87}P_3$: C 79.13, H 10.14; found: C 78.86, H 10.23.

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