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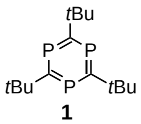
Isolation of a Kinetically Stabilized 1,3,6-Triphosphafulvene[**]

Shigekazu Ito, Hiroki Sugiyama, and
Masaaki Yoshifuji[*]

Substitution of some of the sp^2-hybridized carbon atoms in conjugated systems with heavier main-group elements, such as phosphorus atoms, is of interest but requires kinetic stabilization with bulky substituents. In 1995, 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**) was first reported, prepared through the trimerization of *tert*-butylphosphaacetylene (or 3,3-dimethyl-1-phospha-1-butyne), together with its valence isomer **2**;[1] the structure of **1** was established in 1998.[2, 3] Oligomerization of *tert*-butylphosphaacetylene has been utilized for the construction of various types of five-membered heterocyclic systems containing polycyclic systems.[4] We now report one of the valence isomers of triphosphabenzene, utilizing the 2,4,6-tri-*tert*-butylphenyl group (Mes*). 2,4,6-Tris(2,4,6-tri-*tert*-butylphenyl)-1,3,6-triphosphafulvene (**3**) was formed by the trimerization of lithium phosphanylidene carbenoid **4** (Scheme 1).[5–7]



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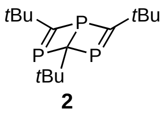

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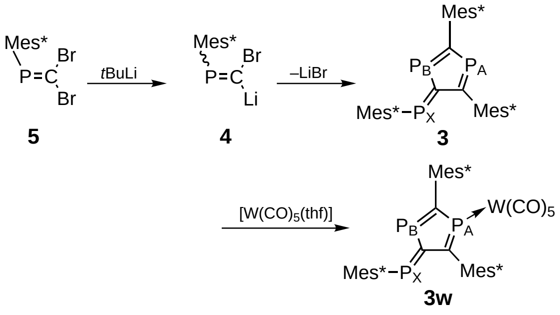
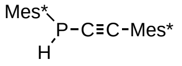


Scheme 1. Preparation of **3** and **3w**. Mes* = 2,4,6-tBu$_3$C$_6$H$_2$.

Dibromophosphaethene **5**[8] was allowed to react with two equivalents of *tert*-butyllithium at −78 °C to afford the phosphanylidene carbenoid **4**, after which the reaction mixture warmed gently to 25 °C. After purification (silica-packed column chromatography), **3** was obtained as a deep red solid together with trace amounts of 2-(2,4,6-tri-*tert*-butylphenyl)-1-(2,4,6-tri-*tert*-butylphenylphosphanyl)acetylene (**6**), 1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaacetylene (**7**),[5–7, 9] and 6,8-di-*tert*-butyl-4,4-dimethyl-1-phospha-3,4-dihydronaphthalene (**8**).[5, 6, 10] The ^{31}P NMR spectrum of **3** shows an ABX system. The signal of the exocyclic phosphorus atom P$_X$ ($\delta_{P_X} = 313.8$) is positioned downfield compared to ring atoms P$_A$ and P$_B$ but similar to that found for **9** ($\delta = 321.5$),[11] due to the electron-withdrawing effects of the 1,3-diphosphacyclopentadiene moiety.[12] The chemical shifts of the ring phosphorus atoms in **3** ($\delta_{P_A} = 291.3$, $\delta_{P_B} = 264.7$) are close to those for 1,2,4-selenadiphosphole **10** (Mch = 1-methylcyclohexyl).[13] Their coupling constant, $J(P_A,P_B)$, is 32 Hz, which is also similar to that found for **10**;[13] values of the exocyclic coupling constants are 120 and 44 Hz for $J(P_A,P_X)$ and $J(P_B,P_X)$, respectively. The UV/Vis spectrum of



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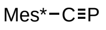

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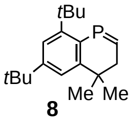

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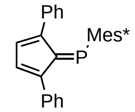

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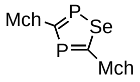

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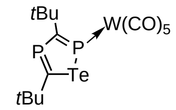

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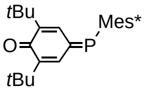

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[*] Prof. Dr. M. Yoshifuji, Dr. S. Ito, H. Sugiyama
Department of Chemistry
Graduate School of Science
Tohoku University
Aoba, Sendai 980-8578 (Japan)
Fax: (+81) 22-217-6562
E-mail: yoshifj@mail.cc.tohoku.ac.jp

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3 has a maxima λ_{max} at 429 nm ($\lg \varepsilon = 3.48$, in hexanes), which is at a longer wavelength than that for **9** ($\lambda_{max} = 358$ nm).[11]

Compound **3** was treated with excess amount of $[W(CO)_5(thf)]$ to afford the pentacarbonyltungsten complex **3w** as a deep red solid (Scheme 1). An ABX system was also observed in the ^{31}P NMR spectrum of **3w** and the signal for the P_A atom shifted remarkably ($\delta_{P_A} = 268.4$) relative to that found in **3**.

Complex **3w** was recrystallized from toluene at 0 °C to afford a suitable crystal for its structural determination. Figure 1 shows an ORTEP drawing of the molecular structure of **3w** together with some selected bond lengths and angles, unambiguously indicating that the metal center coordinates to the P2 (P_A) atom. The exocyclic $\lambda_3\sigma_2$ phosphorus atom takes a *cis* configuration, probably due to the steric congestion. The triphosphafulvene framework (P1 – P3,C1 – C3), W atom, and three *ipso* carbon atoms of the Mes* groups are coplanar to within 0.074(8) Å. This plane lies at angles of 84.5° (P3), 90.0° (C1), and 90.0° (C2) to the mean aromatic rings of the three Mes* groups. The W−P2 distance is 2.480(2) Å, while the P1−C1 and P2−C2 distances (1.689(7) and 1.703(7) Å, respectively) are close to the P=C lengths of tungsten-complexed 1,2,4-telluradiphosphole **11** (1.695(7) and 1.702(7) Å).[14] The P3−C3 distance is 1.710(6) Å, which is close to the P=C length in *p*-phosphaquinone **12** (1.705(2) Å).[15] The C2−C3 distance (1.447(8) Å) is similar to the C−C length in the 1,4-diphospha-1,3-butadiene system.[16] The P1−C3 length (1.815(6) Å) is shorter than the P−C single bond in the straight-chain 1,3-diphospha-1,3-butadiene system.[17] Both of the P−C single bonds in the triphosphafulvene system are shorter than the average $P-C_{sp^2}$ distance (1.836 Å),[18] which indicates the delocalized π system. The C1-P1-C3 and C1-P2-C2 angles are 96.6(3) and 100.2(3)°, respectively, which are smaller than those found in **11** (101.7(3) and 106.3(3)°).[14]

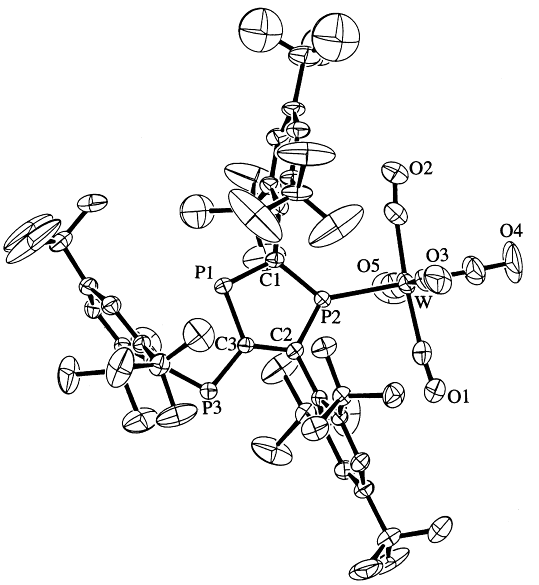
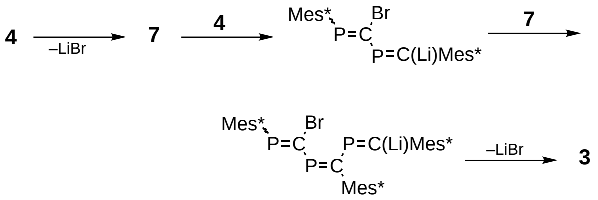


Figure 1. An ORTEP representation of the molecular structure of **3w** with 30 % probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: W-P2 2.480(2), P1-C1 1.689(7), P1-C3 1.815(6), P2-C1 1.801(7), P2-C2 1.703(7), P3-C3 1.710(6), C2-C3 1.447(8), C1-C_{ipso}(Mes*) 1.518(9), C2-C_{ipso}(Mes*) 1.525(8), P3-C_{ipso}(Mes*) 1.857(7); W-P2-C1 129.9(2), W-P2-C2 129.9(2), C1-P1-C3 96.6(3), P1-C1-P2 113.7(4), C1-P2-C2 100.2(3), P2-C2-C3 112.8(4), C2-C3-P1 116.8(5), P1-C3-P3 120.0(3), C2-C3-P3 123.3(5), C3-P3-C_{ipso}(Mes*) 101.7(3).

Compound **3** is regarded as a trimer of the phosphanylidene carbene. As depicted in Scheme 2, phosphaalkyne **7** is first generated from **4** through elimination of LiBr, followed by a [1,2] Fritsch – Buttenberg – Wiechell-type migration.[9] The phosphanylidene carbenoid **4** reacts with two equivalents of **7** in succession and, finally, another LiBr unit was eliminated upon annelation to **3**.[19] The presence of traces of the phosphanylacetylene **6** could be regarded as a reaction product arising from a dimerization of **4** with expulsion of one phosphorus atom.[20]



Scheme 2. Proposed mechanism for the formation of **3**.

As reported previously, after the reaction of dibromophosphaethene **5** with *n*BuLi, **3** was not detected but **8** was obtained as a major product.[10a] Although it is difficult to rationalize this observation on the basis of reactivity differences between *n*BuLi and *t*BuLi,[21] the aggregation of **4** generated with *t*BuLi may be dissimilar as that generated with *n*BuLi. The formation of "free" phosphaalkyne **7** via a [1,2] migration would be preferred if *t*BuLi was employed for the reaction; on the other hand, the intramolecular cyclization would become more facile if *n*BuLi was used. Such effects were observed in the rearrangement reaction to afford phosphaalkyne **7** from (*E*)-2-chloro-1-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaalkene and various butyllithium species.[9a, b]

As stated, 1,3,6-triphosphafulvene **3** is one of the valence isomers of triphosphabenzenes. Compound **3** is deeply colored compared to **1**, which correspond to the properties of fulvene versus benzene.[22] Neither the isomerization of **3** nor the trimerization of **7** affording the corresponding triphosphabenzene derivative has been previously observed. An ab initio calculation (RHF/3-21G* level)[23, 24] on non-substituted systems indicated that 1,3,6-triphosphafulvene is less stable by 20.9 kcal mol^{-1} than 1,3,5-triphosphabenzene. We postulate that the bulky Mes* groups play an important role in controlling the framework of the molecule.

Experimental Section

3: A solution of **5** (500 mg, 1.12 mmol) in THF (40 mL) was treated with *tert*-butyllithium (2.25 mmol, 1.50 mol L^{-1} in *n*-pentane) at −78 °C and allowed to warm to 25 °C. The reaction mixture was stirred for 1 h and the solvent was removed in vacuo. The residue was extracted with *n*-hexane and, in the ^{31}P NMR spectrum of the extract, mainly **3** was observed together with trace amounts of **6**,[25] **7**, and **8**. **3** was isolated by column chromatography (SiO_2, cyclohexane); yield: 57.2 mg (18 %). **3**: Red plates, m.p. 93 – 95 °C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.54$ (m, 2H; H_{arom}), 7.43 (m, 2H; H$_{\text{arom}}$), 7.25 (m, 2H; H$_{\text{arom}}$), 1.45 (s, 18H; o-C(CH$_3$)$_3$), 1.38 (s, 36H; o-C(CH$_3$)$_3$), 1.33 (s, 9H; p-C(CH$_3$)$_3$), 1.28 (s, 9H; p-C(CH$_3$)$_3$), 1.26 (s, 9H; p-C(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): $\delta = 313.8$ (P$_X$), 291.3 (P$_A$), 264.7 (P$_B$) (^2J(P$_A$,P$_B$) = 32, ^2J(P$_A$,P$_X$) = 120, ^3J(P$_B$,P$_X$) = 44 Hz); UV/Vis (hexanes): $\lambda_{\max}$ (lg ε) = 429 nm (3.48); FAB-MS: m/z (%): 864 (19) [M^+], 275 (100) [Mes*P$^+$ − H]. **6**: Colorless needles (MeOH), m.p. 173–174 °C (dec.); ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 7.44$ (d, 2H, ^4J(P,H) = 2.5 Hz; H$_{\text{arom}}$, PMes*), 7.25 (s, 2H; H$_{\text{arom}}$, CMes*), 6.13 (d, 1H, ^1J(P,H) = 244.2 Hz; PH), 1.62 (s, 18H; o-C(CH$_3$)$_3$, PMes*), 1.35 (s, 9H; p-C(CH$_3$)$_3$, PMes*), 1.29 (s, 18H; o-C(CH$_3$)$_3$, CMes*), 1.27 (s, 9H; p-C(CH$_3$)$_3$, CMes*); ^{13}C{^{1}H}-NMR (151 MHz, CDCl$_3$): $\delta = 155.3$ (d, ^2J(P,C) = 9.2 Hz; o-C$_{\text{arom}}$, PMes*), 153.2 (d, ^4J(P,C) = 1.2 Hz; o-C_{arom}, CMes*), 150.2 (s; p-C$_{\text{arom}}$, PMes*), 149.6 (s; p-C_{arom}-CMes*), 124.9 (d, ^1J(P,C) = 24.7 Hz; C$_{\text{ipso}}$, PMes*), 122.3 (d, ^3J(P,C) = 4.3 Hz; m-C$_{\text{arom}}$, PMes*), 120.6 (s; m-C_{arom}, CMes*), 117.4 (s, C$_{\text{ipso}}$, CMes*), 105.3 (s; P−C≡C), 98.7 (d, ^1J(P,C) = 17.3 Hz; P−C≡C), 38.2 (s; o-C(CH$_3$)$_3$-PMes*), 36.3 (s; o-C(CH$_3$)$_3$-CMes*), 35.1 (s; p-C(CH$_3$)$_3$-CMes*), 35.0 (s; p-C(CH$_3$)$_3$, PMes*), 32.6 (d, ^4J(P,C) = 7.2 Hz; o-C(CH$_3$)$_3$, PMes*), 31.4 (s; p-C(CH$_3$)$_3$-PMes*), 31.2 (s; p-C(CH$_3$)$_3$-CMes*), 30.5 (s; o-C(CH$_3$)$_3$-CMes*); ^{31}P NMR (81 MHz, CDCl$_3$): $\delta = -98.6$ (d, ^1J(P,H) = 244.2 Hz); IR (KBr): $\tilde{\nu} = 2378, 2148$ cm^{-1}; MS (70 eV, EI): m/z (%): 546 (69) [M^+], 489 (100) [M^+ − tBu]; elemental analysis calcd for C$_{38}$H$_{59}$P: C 83.46, H 10.87; found: C 82.68, H 10.99.

3w: A solution of **3** (30.7 mg, 35.5 μmol) in THF (5 mL) was treated with [W(CO)$_5$(thf)] (about 0.143 mmol, prepared in situ by irradiation of a THF solution of [W(CO)$_6$] for 8 h with a medium-pressure Hg lamp). The reaction mixture was stirred for 12 h and the solvent was removed in vacuo. The residue was treated with column chromatography (SiO$_2$, n-hexane) affording **3w** as deep red crystals. Yield 5.5 mg (13%); m.p. 176–179 °C (dec.); ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 7.54$ (m, 2H; H$_{\text{arom}}$), 7.43 (m, 2H; H$_{\text{arom}}$), 7.25 (m, 2H; H$_{\text{arom}}$) 1.45 (s, 18H; o-C(CH$_3$)$_3$), 1.37 (s, 36H; o-C(CH$_3$)$_3$), 1.33 (s, 9H; p-C(CH$_3$)$_3$), 1.28 (s, 9H; p-C(CH$_3$)$_3$), 1.26 (s, 9H; p-C(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): $\delta = 318.7$ (P$_X$), 268.4 (P$_A$), 260.4 (P$_B$) (J(P$_A$,P$_B$) = 54, J(P$_A$,P$_X$) = 140, J(P$_B$,P$_X$) = 71, J(P$_A$,W) = 277 Hz); IR (KBr): $\tilde{\nu} = 2071, 1944$ cm^{-1}; FAB-MS: m/z (%): 1188 (2) [M^+ + H], 864 (13) [M^+ − W(CO)$_5$], 545 (100) [Mes*$_2$C$_2$P$^+$].

Crystal data for **3w** (C$_{62}$H$_{87}$O$_5$P$_3$W): $M_r = 1189.14$, deep red prisms crystallized from toluene at 0 °C, dimensions $0.30 \times 0.20 \times 0.20$ mm^3, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.776(5)$, $b = 20.961(2)$, $c = 28.372(5)$ Å, $\beta = 91.43(3)°$, $V = 6406(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.233$ g cm^{-3}, $F(000) = 2472.00$, $\mu = 1.923$ mm^{-1}, $T = 298(1)$ K. A Rigaku RAXIS-IV imaging plate detector with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) was used. Of 9153 reflections measured ($2\theta_{\max} = 50.0°$), 6240 were observed ($I > 3.0\sigma(I)$). The structure was solved by direct methods (SIR92),[26] expanded using Fourier techniques (DIRDIF94),[27] and refined by full-matrix least squares on F for 628 variable parameters. The non-hydrogen atoms, except the disordered C atoms, were refined anisotropically. The disordered C atoms of the methyl groups at the p-position of the C1-bonded Mes* group were refined isotropically. Hydrogen atoms were included but not refined. $R = 0.049$ for $I > 3.0\sigma(I)$ and $R_w = 0.110$ for all data. Goodness of fit $S = 1.30$ for all observed reflections. Max./min. electron density = 0.77/−0.73 e Å^{-3}. Structure solution, refinement, and graphical representation were carried out using the teXsan package.[28] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140669. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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