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

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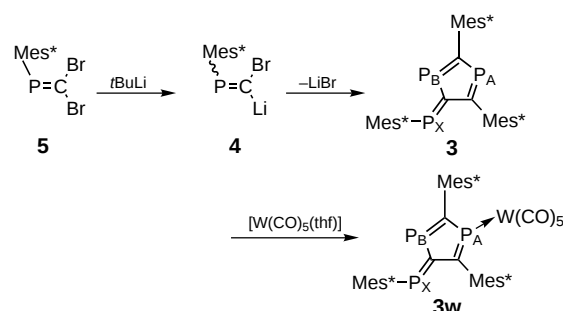
Substitution of some of the sp²-hybridized carbon atoms in conjugated systems with heavier main-group elements, such as phosphorus atoms, is of interest but requires kinetic stabilization with bulky substituents. In 1995, 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**) was first reported, prepared through



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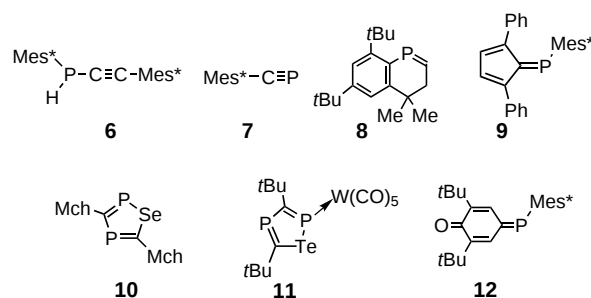
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the trimerization of *tert*-butylphosphaacetylene (or 3,3-dimethyl-1-phospha-1-butyne), together with its valence isomer **2**;^[1] the structure of **1** was established in 1998.^[2, 3] Oligomerization of *tert*-butylphosphaacetylene has been utilized 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 phosphanidene carbenoid **4** (Scheme 1).^[5–7]



Scheme 1. Preparation of **3** and **3w**. Mes* = 2,4,6-*t*Bu₃C₆H₂.

Dibromophosphaethene **5**^[8] was allowed to react with two equivalents of *tert*-butyllithium at –78 °C to afford the phosphanidene 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 ³¹P NMR spectrum of **3**



shows an ABX system. The signal of the exocyclic phosphorus atom P_X (δ_{P_X} = 313.8) is positioned downfield compared to ring atoms P_A and P_B but similar to that found for **9** (δ = 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** (δ_{P_A} = 291.3, δ_{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

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

Compound **3** was treated with excess amount of $[\text{W}(\text{CO})_5(\text{thf})]$ 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 ($\delta_\text{PA} = 268.4$) 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

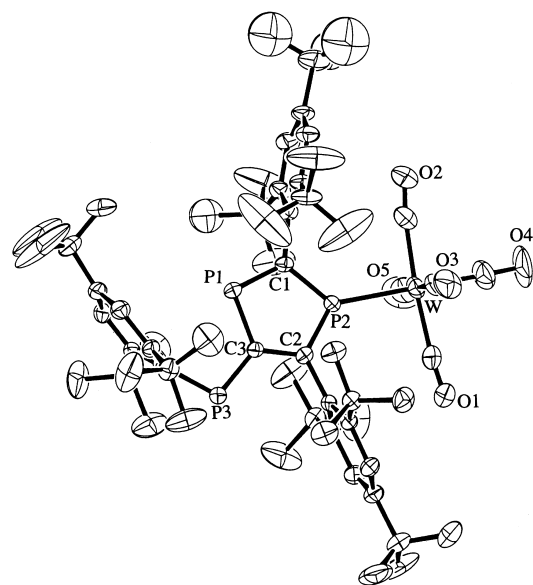
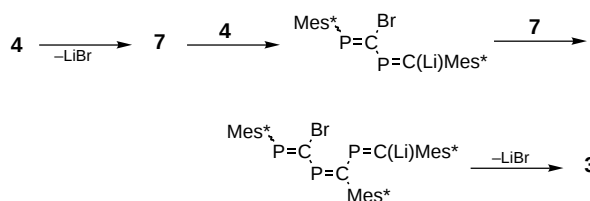


Figure 1. An ORTEP representation of the molecular structure of **3w** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles $^\circ$: W–P2 2.480(2), P1–C1 1.689(7), P1–C3 1.815(6), P2–C1 1.801(7), P2–C2 1.703(7), P3–C3 1.710(6), C2–C3 1.447(8), 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).

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_{sp²} 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) $^\circ$, respectively, which are smaller than those found in **11** (101.7(3) and 106.3(3) $^\circ$).^[14]

Compound **3** is regarded as a trimer of the phosphanylidene carbene. As depicted in Scheme 2, phosphalkyne **7** is first generated from **4** through elimination of LiBr, followed by a



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

[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]

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” phosphalkyne **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 phosphalkyne **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 triphosphabenzene. 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 (SiO₂, cyclohexane); yield: 57.2 mg (18%). **3**: Red plates, m.p. $93-95^\circ\text{C}$ (dec.); ^1H NMR (200 MHz, CDCl₃): $\delta = 7.54$ (m, 2H; H_arom),

7.43 (m, 2H; H_{arom}), 7.25 (m, 2H; H_{arom}), 1.45 (s, 18H; $o\text{-C}(\text{CH}_3)_3$), 1.38 (s, 36H; $o\text{-C}(\text{CH}_3)_3$), 1.33 (s, 9H; $p\text{-C}(\text{CH}_3)_3$), 1.28 (s, 9H; $p\text{-C}(\text{CH}_3)_3$), 1.26 (s, 9H; $p\text{-C}(\text{CH}_3)_3$); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): $\delta = 313.8$ (P_X), 291.3 (P_A), 264.7 (P_B) ($^2J(P_A, P_B) = 32$, $^3J(P_A, P_X) = 120$, $^3J(P_B, P_X) = 44$ Hz); UV/Vis (hexanes): λ_{max} (lg ϵ) = 429 nm (3.48); FAB-MS: m/z (%): 864 (19) [M^+], 275 (100) [$\text{Mes}^*\text{P}^+ - \text{H}$]. **6**: Colorless needles (MeOH), m.p. 173–174 °C (dec.); ^1H NMR (200 MHz, CDCl_3): $\delta = 7.44$ (d, 2H, $^4J(P, H) = 2.5$ Hz; H_{arom} , PMes^*), 7.25 (s, 2H; H_{arom} , CMes^*), 6.13 (d, 1H, $^1J(P, H) = 244.2$ Hz; PH), 1.62 (s, 18H; $o\text{-C}(\text{CH}_3)_3$, PMes^*), 1.35 (s, 9H; $p\text{-C}(\text{CH}_3)_3$, PMes^*), 1.29 (s, 18H; $o\text{-C}(\text{CH}_3)_3$, CMes^*), 1.27 (s, 9H; $p\text{-C}(\text{CH}_3)_3$, CMes^*); $^{13}\text{C}\{^1\text{H}\}$ -NMR (151 MHz, CDCl_3): $\delta = 155.3$ (d, $^2J(P, C) = 9.2$ Hz; $o\text{-C}_{\text{arom}}$, PMes^*), 153.2 (d, $^4J(P, C) = 1.2$ Hz; $o\text{-C}_{\text{arom}}$, CMes^*), 150.2 (s; $p\text{-C}_{\text{arom}}$, PMes^*), 149.6 (s; $p\text{-C}_{\text{arom}}$ - CMes^*), 124.9 (d, $^1J(P, C) = 24.7$ Hz; C_{ipso} , PMes^*), 122.3 (d, $^3J(P, C) = 4.3$ Hz; $m\text{-C}_{\text{arom}}$, PMes^*), 120.6 (s; $m\text{-C}_{\text{arom}}$, CMes^*), 117.4 (s, C_{ipso} , CMes^*), 105.3 (s; $P\text{-C}\equiv\text{C}$), 98.7 (d, $^1J(P, C) = 17.3$ Hz; $P\text{-C}\equiv\text{C}$), 38.2 (s; $o\text{-C}(\text{CH}_3)_3\text{-PMes}^*$), 36.3 (s; $o\text{-C}(\text{CH}_3)_3\text{-CMes}^*$), 35.1 (s; $p\text{-C}(\text{CH}_3)_3\text{-CMes}^*$), 35.0 (s; $p\text{-C}(\text{CH}_3)_3$, PMes^*), 32.6 (d, $^4J(P, C) = 7.2$ Hz; $o\text{-C}(\text{CH}_3)_3$, PMes^*), 31.4 (s; $p\text{-C}(\text{CH}_3)_3\text{-PMes}^*$), 31.2 (s; $p\text{-C}(\text{CH}_3)_3\text{-CMes}^*$), 30.5 (s; $o\text{-C}(\text{CH}_3)_3\text{-CMes}^*$); ^{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) [$M^+ - t\text{Bu}$]; elemental analysis calcd for $\text{C}_{38}\text{H}_{50}\text{P}$: 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 $[\text{W}(\text{CO})_5(\text{thf})]$ (about 0.143 mmol, prepared in situ by irradiation of a THF solution of $[\text{W}(\text{CO})_6]$ 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.); ^1H NMR (200 MHz, CDCl_3): $\delta = 7.54$ (m, 2H; H_{arom}), 7.43 (m, 2H; H_{arom}), 7.25 (m, 2H; H_{arom}), 1.45 (s, 18H; $o\text{-C}(\text{CH}_3)_3$), 1.37 (s, 36H; $o\text{-C}(\text{CH}_3)_3$), 1.33 (s, 9H; $p\text{-C}(\text{CH}_3)_3$), 1.28 (s, 9H; $p\text{-C}(\text{CH}_3)_3$), 1.26 (s, 9H; $p\text{-C}(\text{CH}_3)_3$); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): $\delta = 318.7$ (P_X), 268.4 (P_A), 260.4 (P_B) ($^2J(P_A, P_B) = 54$, $^3J(P_A, P_X) = 140$, $^3J(P_B, P_X) = 71$, $^4J(P_A, W) = 277$ Hz); IR (KBr): $\tilde{\nu} = 2071$, 1944 cm^{-1} ; FAB-MS: m/z (%): 1188 (2) [$M^+ + \text{H}$], 864 (13) [$M^+ - \text{W}(\text{CO})_5$], 545 (100) [$\text{Mes}^*_2\text{C}_2\text{P}^+$].

Crystal data for **3w** ($\text{C}_{62}\text{H}_{87}\text{O}_5\text{P}_3\text{W}$): $M_r = 1189.14$, deep red prisms crystallized from toluene at 0 °C, dimensions 0.30 $\times$ 0.20 $\times$ 0.20 mm³, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.776(5)$, $b = 20.961(2)$, $c = 28.372(5)$ Å, $\beta = 91.43(3)^\circ$, $V = 6406(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.233$ 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 MoK_α radiation ($\lambda = 0.71070$ Å) was used. Of 9153 reflections measured ($2\theta_{\text{max}} = 50.0^\circ$), 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 Cl-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 = 0.771/–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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