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Synthesis of pentacarbonyltungsten(0) complexes of bulky 1,2-diphosphabut-1-en-3-ynes as a heavier enyne congener

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Abstract—Pentacarbonyltungsten(0) complexes of kinetically stabilized 1,2-diphosphabut-1-en-3-ynes were synthesized as a heavier conjugated enyne system featuring a phosphorus–phosphorus double bond, and characterized by spectroscopic and crystallographic analyses.

Considerable attention is being paid to ethynylphosphines [>P–C≡C–] because of the electronic interaction between the phosphorus atom and the π-orbital of the acetylene moiety. It has been known that ethynylphosphines show certain changes in spectroscopic and thermodynamic properties as well as interconversion of the skeleton,[1–5] and they have been utilized as a source of some organometallic and cyclic compounds.[6–9] On the other hand, in 1981, we reported the first successful example of a stable diphosphene **1** (Chart 1) by use of a kinetic stabilization method with a bulky 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Mes*),[10] and until now, a number of stable diphosphenes have been derived as described in the reviews.[11–14] Although the diphosphene moiety can be incorporated with any conjugated system, the number of conjugated systems involving the P=P unit is quite limited if those with directly bound aromatic rings are excluded.[11,15–17] Taking these results into consideration, substitution of the acetylene group on the low-coordinated phosphorus atom would affect the intriguing properties of the diphosphene moiety, which would be utilized as a material for novel conjugated systems including low-coordinated phosphorus atoms, since conjugated enyne compounds indicate versatile properties for organic synthesis[18] and antibiotics.[19] Here we report the preparation, structure and some properties of kinetically stabilized 1,2-diphosphabut-1-en-3-yne compounds (**2**), ligating on the tungsten(0) pentacarbonyl.

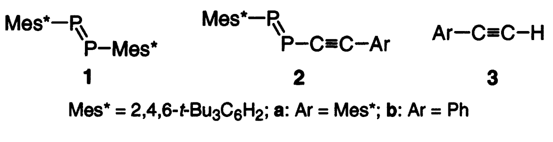
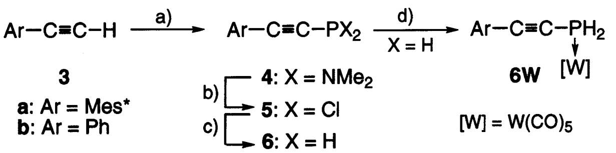


Chart 1.

Taking into account the expected large protecting effect of the Mes* group, we first chose 1,3,5-tri-*t*-butyl-2-ethynylbenzene (**3a**)[20] as the starting acetylene for ethynylphosphines **4a**–**6a**, and then ethynylbenzene (**3b**) for the series of **4b**–**6b**, as shown in Scheme 1.[7] The acetylenes **3** were derived to acetylides, followed by treatment with chlorobis(dimethylamino)phosphine to give the corresponding diaminophosphines **4** almost quantitatively.[21] Compounds **4** were treated with hydrogen chloride in ether to give dichlorophosphines **5**, and **5** was allowed to react with lithium aluminum hydride to afford primary phosphines **6** almost quantitatively.[21] Although bulky phosphine **6a** was an air- and moisture-sensitive colorless solid, its polymerization was avoided probably due to the bulky substituents. Phosphine **6b** was isolated without decomposition by extraction with ether.[22]



Scheme 1. Preparations of ethtynylphosphines. *Reagents and conditions*: (a) (1) *n*-BuLi/THF/−78°C, (2) ClP(NMe$_2$)$_2$; (b) HCl/Et$_2$O/−78 to 15°C; (c) LiAlH$_4$/Et$_2$O/−78°C; (d) W(CO)$_5$(THF)/THF.

Keywords: phosphorus compounds; diphosphenes; alkynes; complexes; steric effects.

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Next, attempts were made to prepare diphosphene **2a** by a similar preparative method for unsymmetrical diphosphene **7**,[23] but either from combination of **5a** and **8**–**10** or **6a** and **11** (Chart 2), the attempts failed to give **2a**, and the decomposition of **5a** and **6a** was observed. Accordingly, we tried to prepare **2a** in a complexed form. Thus, **6a** was allowed to react with an equivalent amount of $W(CO)_5(THF)$ to afford the corresponding complex **6aW**[21] in 35% isolated yield after SiO_2 column chromatography as an air-stable orange solid (Scheme 2). According to the method for complex **7W**,[24] complex **6aW** was allowed to react with dichlorophosphine **11** in the presence of DBU (diazabicyclo[5.4.0]undec-7-ene) to give the corresponding carbonyltungsten complex **2aW**[25] as an air-stable orange solid. Complex **2aW** was isolated after SiO_2 column chromatography (hexane) followed by gel permeation chromatography (chloroform) in 20% yield from **3a** (Scheme 2). Moreover, complex **6bW**, prepared in a similar manner, afforded the corresponding diphosphene complex **2bW**[25] in 10% isolated yield from **3b** (Scheme 2). Complex **2bW** can be handled in air, although it decomposes on an SiO_2 column. It seems likely that the bulky Mes* group as a substituent on the acetylene is not essential for stabilization of either **2W** or **6W**. On the other hand, the reaction of **5** with phosphine complex **8W** did not give the diphosphene complex, probably due to the steric encumbrance.

^{31}P NMR spectra of **2W** display a typical AB pattern, which is similar to diphosphene complex **7W**,[24] indicating an *E*-configuration from its chemical shifts and an end-on coordination on $W(CO)_5$ from its J_{PW} values.[26] UV–vis spectra of **2W** show longer λ_{max} values [457 nm (**2aW**), 462 nm (**2bW**)] than that for **7W** (436 nm),[24] probably due to the effect of the acetylene unit on the extended conjugation.

The structures of **2aW** and **2bW** were confirmed by X-ray crystallographic analyses, as shown in Figs. 1 and 2.[27] The C_{Mes*}–P=P(W)–C≡C–C_{Ar} systems are planar. The P–W distances of **2aW** and **2bW** are both 2.475 Å, which are comparable to those of **12** [2.456(2) Å][28] and **13** (Chart 3) [2.484(3) and 2.491(3) Å].[29] The complex **2bW** showed the longest P=P bond length [2.049(3) Å] ever reported for diphosphenes, i.e. **1** [2.034(2) Å],[10] **12** [2.025(3) Å],[28] **13** [2.041(4) Å],[29] and the present **2aW** (2.037(4) Å). The Mes* ring on the phosphorus atom is almost perpendicular to the C_{Mes*}–P=P(W)–C≡C–C_{Ar} plane (Ar = Mes* or Ph) [C_{Mes*}–P1–P2(W)–C1–C2–C_{Ar} versus Mes*(P): 85.4(3)° for **2aW** and 89.6(4)° for **2bW**], suggesting its sterically effective protection of the P=P skeleton. On the contrary, the Ar ring on the acetylene unit is considerably planar to the C_{Mes*}–P=P(W)–C≡C–C_{Ar} plane [C_{Mes*}–P=P(W)–C≡C–C_{Ar} versus Ar(C): 19.7(3)° for **2aW** and 12.2(2)° for **2bW**], in contrast to the average torsion angle of 64° observed for **1** in the solid state.[10,11] Steric congestion around the P2 atom in **2aW** or **2bW** is released due to an acetylene spacer, and the aromatic ring on the acetylene side apparently tends to take co-planarity with the P=P–C≡C group.

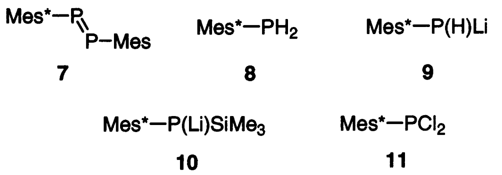
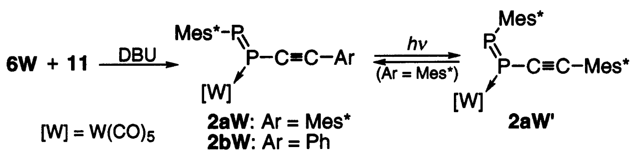


Chart 2.



Scheme 2. Preparation of diphosphene complexes **2W**.

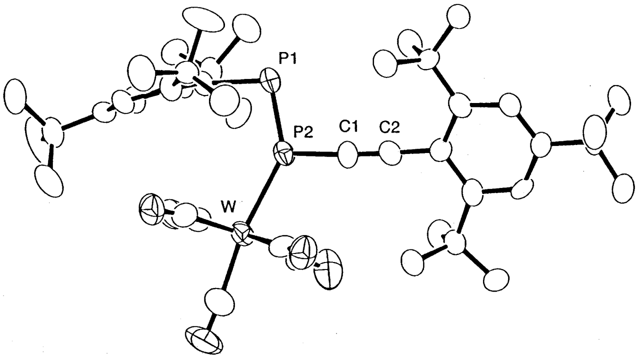


Figure 1. An ORTEP drawing of the molecular structure of **2aW**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P2–W 2.475(3), P1–P2 2.038(4), P1–C(Mes*) 1.829(10), P2–C1 1.745(10), C1–C2 1.19(1), C2–C(Mes*) 1.43(1), C(Mes*)–P1–P2 97.3(3), P1–P2–C1 101.3(4), P1–P2–W 142.5(1), C1–P2–W 116.0(4), P2–C1–C2 175.8(9), C1–C2–C(Mes*) 177.3(10).

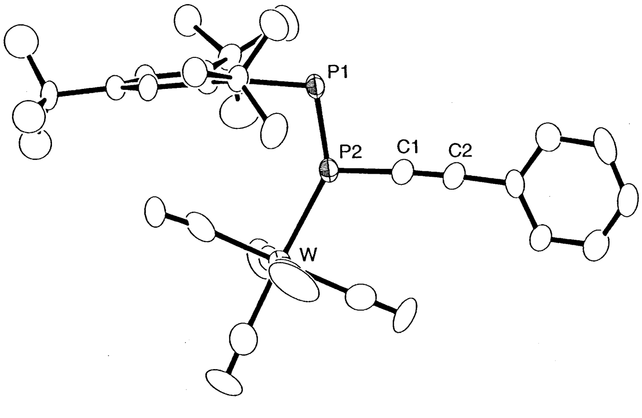
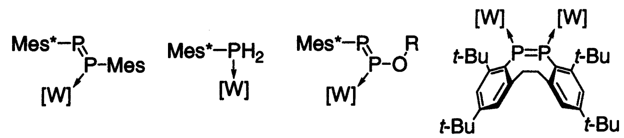


Figure 2. An ORTEP drawing of the molecular structure of **2bW**. Hydrogen atoms are omitted for clarity. The *p*-*t*-butyl group in the Mes* group is disordered and the atoms with a predominant occupancy factor (0.57), which is refined isotropically, are shown. Selected bond lengths (Å) and angles (°): P2–W 2.475(2), P1–P2 2.049(3), P1–C(Mes*) 1.855(7), P2–C1 1.739(7), C1–C2 1.21(1), C2–C(Mes*) 1.448(10), C(Mes*)–P1–P2 102.9(2), P1–P2–C1 98.8(3), P1–P2–W 143.4(1), C1–P2–W 116.8(3), P2–C1–C2 175.6(7), C1–C2–C(Mes*) 175.5(8).



7W **8W** **12** **13**

R = 2,6-*t*-Bu_2-4-MeC_6H_2

Chart 3.

Diphosphene complex **2aW** was isomerized by photoirradiation. Complex **2aW** in benzene-d_6 was irradiated with a medium-pressure mercury lamp through a Pyrex filter to afford an *E*/*Z* mixture in a 4:1 ratio after 3 days, as shown in Scheme 2. The *Z*-isomer (**2aW′**) displays an AB pattern with a higher ^{31}P chemical shift and a larger $^{1}J_{PP}$ value than those for the *E*-isomer [**2aW′**: δ_P 268, 388 ($^{1}J_{PW}$ 254 Hz), $^{1}J_{PP}$ 549 Hz].[30] Attempts to obtain free diphosphene **2a** by decomplexation of **2aW** are now in progress.

Acknowledgements

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21. *NMR data.* **4a**: $^{31}P\{^{1}H\}$ NMR (81 MHz, CD_2Cl_2) δ 76.2; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 1.34 (9H, s, *p*-*t*-Bu), 1.58 (18H, s, *o*-*t*-Bu), 2.85 (12H, d, $^{4}J_{HH}$ 12 Hz, NMe_2), 7.37 (2H, s, arom); $^{13}C\{^{1}H\}$ NMR (50 MHz, CD_2Cl_2) δ 103.5 (d, $^{1}J_{PC}$ 16 Hz, P*C*≡C), 107.6 (d, $^{2}J_{PC}$ 7 Hz, PC≡*C*). **5a**: $^{31}P\{^{1}H\}$ NMR (81 MHz, CD_2Cl_2) δ 123.0; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 1.35 (9H, s, *p*-*t*-Bu), 1.58 (18H, s, *o*-*t*-Bu), 7.24 (2H, s, arom); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) δ 99.3 (d, $^{1}J_{PC}$ 75 Hz, P*C*≡C), 118.1 (d, $^{2}J_{PC}$ 5 Hz, PC≡*C*). **6a**: ^{31}P NMR (81 MHz, CD_2Cl_2) δ −176.0 (t, $^{1}J_{PH}$ 214 Hz); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.34 (9H, s, *p*-*t*-Bu), 1.55 (18H, s, *o*-*t*-Bu), 3.95 (2H, d, $^{1}J_{PH}$ 214 Hz, PH_2), 7.36 (2H, s, arom); $^{13}C\{^{1}H\}$ NMR (50 MHz, CD_2Cl_2) δ 90.2 (d, $^{1}J_{PC}$ 9 Hz, P*C*≡C), 106.1 (d, $^{2}J_{PC}$ 2 Hz, PC≡*C*). **6aW**: $^{31}P\{^{1}H\}$ NMR (81 MHz, CD_2Cl_2) δ −139.0 (t, $^{1}J_{PH}$ 373 Hz; $^{1}J_{PW}$ 228 Hz); ^{1}H NMR (200 MHz, CD_2Cl_2) δ 1.35 (9H, s, *p*-*t*-Bu), 1.57 (18H, s, *o*-*t*-Bu), 5.40 (2H, d, $^{1}J_{PH}$ 373 Hz, PH_2), 7.40 (2H, s, arom); $^{13}C\{^{1}H\}$ NMR (50 MHz, CD_2Cl_2) δ 86.3 (d, $^{1}J_{PC}$ 86 Hz, P*C*≡C), 109.1 (d, $^{2}J_{PC}$ 13 Hz, PC≡*C*).
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25. *Selected physical data.* **2aW**: Orange prisms (hexane), mp 164–166°C; $^{31}P\{^{1}H\}$ NMR (81 MHz, CD_2Cl_2) δ 277.0, 470.0, ($^{1}J_{PW}$ 257 Hz), $^{1}J_{PP} = 468$ Hz; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 1.38 (9H, s, *p*-*t*-Bu), 1.39 (9H, s, *p*-*t*-Bu), 1.57 (18H, s, *o*-*t*-Bu), 1.66 (18H, s, *o*-*t*-Bu), 7.45 (2H, brs, Mes*), 7.53 (2H, s, Mes*); $^{13}C\{^{1}H\}$ NMR (50 MHz, CD_2Cl_2) δ 108.0 (dd, $^{1}J_{PC}$ 36 Hz, $^{2}J_{PC}$ 29 Hz, P–*C*≡C), 115.8 (m, P–C≡*C*); UV–vis (CH_2Cl_2) λ_{max} (log ε) 457 nm (3.98). Anal. calcd for $C_{43}H_{58}O_5P_2W$: C, 56.91; H, 6.94. Found: C, 57.34; H, 6.49%. **2bW**: Orange prisms (toluene), mp 165–169°C; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 273.1$, 465.9 ($^{1}J_{PW}$ 252 Hz), $^{1}J_{PP}$ 467 Hz; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (9H, s, *p*-*t*-Bu), 1.54 (18H, s, *o*-*t*-Bu), 7.53 (2H, s, Mes*), 7.2–7.7 (5H, m, Ph); UV–vis (CH_2Cl_2) λ_{max} (log ε) 462 nm (3.89). HRMS (EI) calcd for $C_{31}H_{34}O_5P_2W$: *m*/*z* 732.1391. Found: *m*/*z* 732.1393.
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27. *Crystal data.* **2aW**: $C_{43}H_{58}O_5P_2W$, $M = 900.73$, triclinic, $P\bar{1}$ (#2), $a = 14.530(4)$, $b = 15.24(1)$, $c = 11.712(4)$ Å, $\alpha = 106.26(5)$, $\beta = 111.15(2)$, $\gamma = 100.64(4)°$, $V = 2200(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.36$ g cm^{-1}, $\mu(MoK_\alpha) = 2.74$ mm^{-1}, $T = 140$ K, 6780 total reflections, 6490 unique reflec-

tions [$I>2.0\sigma(I)$], 2θ max = 50.1°, $R1 = 0.072$, $R_W = 0.115$ (all data), $S = 1.58$ for 464 parameters (CCDC 176662). **2bW**: $C_{31}H_{34}O_5P_2W$, $M = 732.40$, triclinic, $P\bar{1}$ (#2), $a = 11.750(2)$, $b = 15.57(1)$, $c = 9.672(3)$ Å, $\alpha = 98.52(3)$, $\beta = 113.04(2)$, $\gamma = 76.33(3)°$, $V = 1578(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.54$ g cm^{-1}, $\mu(MoK_\alpha) = 3.80$ mm^{-1}, $T = 140$ K, 4880 total reflections, 4642 unique reflections [$I>2.0\sigma(I)$], 2θ max = 50.1°, $R1 = 0.050$, $R_W = 0.129$ (all data), $S = 1.27$ for 350 parameters (CCDC 178461).

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