

Application of 1,2-Bis(2-bromo-3,5-di-*t*-butylphenyl)ethane to Preparation of Compounds Having Two Diphosphene Units

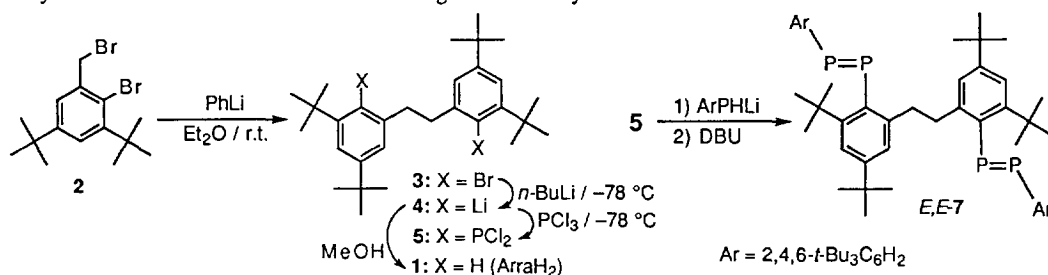
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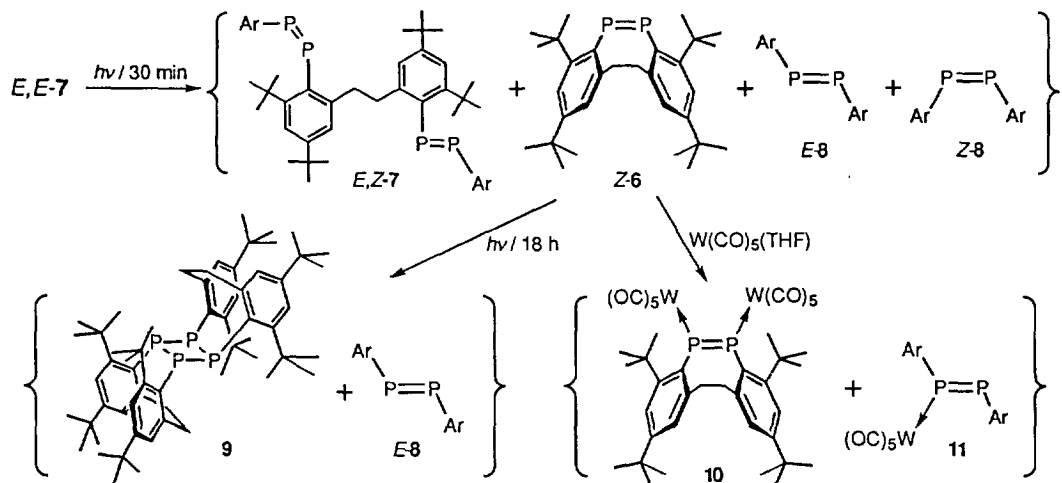
Abstract: A sterically crowded bromobenzene, 1,2-bis(2-bromo-3,5-di-*t*-butylphenyl)ethane, was prepared and converted to the corresponding phosphonous dichloride, which reacted with lithium (2,4,6-tri-*t*-butylphenyl)phosphide to give 1,2-bis[3,5-di-*t*-butyl-2-[(2,4,6-tri-*t*-butylphenyl)phosphinidene(diphosphino)phenyl]ethane; the photolysis of the compound gave *E*-bis(2,4,6-tri-*t*-butylphenyl)diphosphene and an internal *Z*-diphosphene; the tungsten complex of the latter was analyzed by X-ray crystallography. Copyright © 1996 Elsevier Science Ltd

Compounds with low coordinated heavier main group elements such as phosphorus are of current interest.¹ The 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar) is one of the most powerful protecting groups and by utilizing this substituent we have been successful in the first preparation of diphosphenes.^{2,3} We report here on the utilization of 1,2-bis(2-bromo-3,5-di-*t*-butylphenyl)ethane (**3**)⁴ for preparation of compounds containing two diphosphene units within one molecule.

2-Bromo-1-(bromomethyl)-3,5-di-*t*-butylbenzene (**2**) was prepared according to the method reported previously.⁵ Reaction of **2** with phenyllithium afforded a homo-coupling product **3**. To a solution of **2** (2.991 g, 8.26 mmol) in ether (40 mL) was added 4.24 mmol of phenyllithium (1.01 M in cyclohexane-ether) at room temperature and the resulting solution was stirred for 30 min. The reaction mixture was worked up as usual and recrystallization from hexane afforded 1.487 g of **3** in 64% yield.⁶



Lithiation of **3** in THF with butyllithium at -78 °C led to the formation of dilithio derivative **4**, which was quenched with methanol to give **1** (abbreviated to ArraH₂)⁷ in 67% yield. When **4** was allowed to react with phosphorus trichloride, 1,2-bis[3,5-di-*t*-butyl-2-(dichlorophosphino)phenyl]ethane (**5**) was obtained. To a solution of **3** (236.5 mg, 0.419 mmol) in THF (10 mL) was added 0.924 mmol of butyllithium (1.68 M in hexane) at -78 °C, then 2.12 mmol of phosphorus trichloride was added, and the resulting mixture was warmed to room temperature to give **5** as a pentane-insoluble material (182.3 mg, 72%).⁶ Attempts to prepare an internal diphosphene **6** from **5** with either magnesium metal, *t*-butyllithium, or lithium naphthalenide as a coupling reagent,¹ were not successful. But preparation of a compound containing two diphosphene units was successful. To a solution of ArPH₂ (100.0 mg, 0.36 mmol) in THF (10 mL) was added 0.36 mmol of



butyllithium (1.64 M in hexane) at $-78\text{ }^\circ\text{C}$ and the resulting solution of lithium (2,4,6-tri-*t*-butylphenyl)phosphide ($ArPHLi$)⁸ was added dropwise to a THF (100 mL) solution of **5** (153.1 mg, 0.25 mmol) over a 15-min period at $-78\text{ }^\circ\text{C}$. Then the mixture was warmed to room temperature and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 80 μL , 0.53 mmol) was added to the solution at $0\text{ }^\circ\text{C}$. After usual workup, 1,2-bis[3,5-di-*t*-butyl-2-[(2,4,6-tri-*t*-butylphenyl)phosphinidenephosphino]phenyl]ethane (*E,E*-7; 37.3 mg)⁶ was obtained in 20% yield based on $ArPH_2$.

On the other hand, we and others have reported on generation of the symmetrical diphosphene **8** during the photolysis of some unsymmetrical diphosphenes such as $ArP=PMe$,⁹ 2,4,6-(CF_3)₃ $C_6H_2P=PAr$,¹⁰ or (Me_5C_5) $P=PAr$.¹¹ When a benzene-*d*₆ solution of the diphosphene *E,E*-7 was irradiated with a 500-W Xe-lamp through a Toshiba Y-49 filter at room temperature for 30 min, a mixture consisting of *E,Z*-7,⁶ *E*-8 ($\delta_P = 494$),¹ *Z*-8 ($\delta_P = 370$),^{12,13} and an internal *Z*-diphosphene *Z*-6 ($\delta_P = 394$) together with *E,E*-7 was obtained in a molar ratio of 48:10:1:10:17, respectively.¹⁴ Upon 18-h irradiation of *E,E*-7 (86.8 mg, 0.0851 mmol), however, *E*-8 (almost quantitative yield) and a cyclotetraphosphane **9** (24.3 mg, 0.026 mmol)⁶ were isolated. In a separate experiment, when a THF solution of an excess amount of $W(CO)_5(THF)$ was added to a photolysis mixture of *E,E*-7 (46.1 mg, 0.0452 mmol) after 30-min irradiation, [*Z*-6][$W(CO)_5$]₂ (**10**)⁶ was isolated as red crystals (3.4 mg, 7% yield) together with [*E*-8][$W(CO)_5$] (**11**) as the major product (*ca.* 20% yield).^{6,15} The structure of the complex **10** was unambiguously confirmed by X-ray crystallography.¹⁶ Figure 1 shows a molecular structure drawing of **10** and the structure is similar to that of [(*Z*)-Mes-P=P-Ar]Cr(CO)₅¹⁷ or, more likely, to that of [(*Z*)-Mes-P=P-Mes][Mo(CO)₅]₂.¹⁸ The P–P bond length is 2.041(4) Å and is similar to 2.034(2) Å for *E*-8, 2.039(3) Å for [(*Z*)-Mes-P=P-Ar]Cr(CO)₅, and 2.026(2) Å for [(*Z*)-Mes-P=P-Mes][Mo(CO)₅]₂. The dihedral angle $\angle C(1)–P(1)–P(2)–C(7)$ is $-2.0(5)^\circ$, indicating that the *Z*-diphosphene system [C(1),P(1),P(2),C(7)] is coplanar within 0.03(1) Å, while the atoms [W(1),P(1),P(2),W(2)] form another plane within 0.030(3) Å, making a dihedral angle of 15.8° to each other. Two phenyl rings are planar within 0.02 Å, respectively, faced at a dihedral angle of 51.1° . The atoms [C(6),C(21),C(30),C(12)] are coplanar within 0.03 Å, indicating the ethylene bridge takes an eclipsed conformation. Some important bond lengths and angles are shown in the caption to Fig. 1.

While Niecke *et al.* has reported an amino-stabilized *Z*-diphosphene,¹⁹ during the photolysis of *E,E*-7 an olefin-metathesis type of reaction²⁰ occurred to give an internal *Z*-diphosphene **6** as well as **8**. Furthermore,

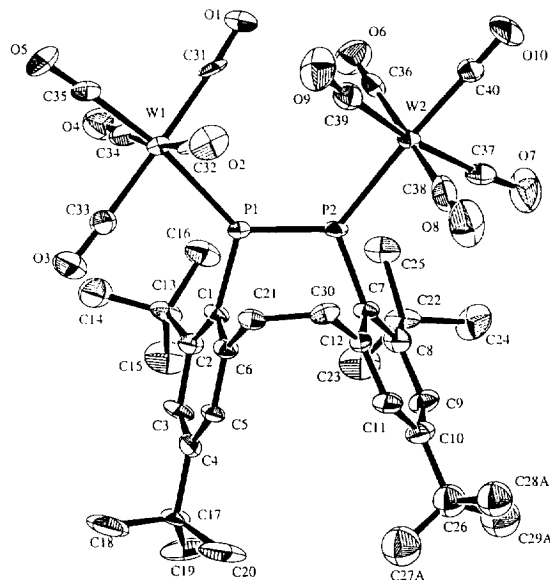


Figure 1. Molecular structure for **10** showing atom labeling scheme. The methyl groups C27–C29 are disordered but only the structure with major occupancy factor is displayed. Hydrogen atoms are omitted for clarity. Some important bond lengths and angles: W(1)–P(1), 2.491(3); P(1)–P(2), 2.041(4); P(1)–C(1), 1.835(10); W(2)–P(2), 2.484(3); W(1)–P(1), 2.491(3); P(2)–C(7), 1.83(1); W(1)–P(1)–P(2), 131.2(1); W(1)–P(1)–C(1), 120.9(4); P(2)–P(1)–C(1), 105.7(4); W(2)–P(2)–P(1), 129.3(1); W(2)–P(2)–C(7), 119.3(4); P(1)–P(2)–C(7), 109.9(4); C(6)–C(21)–C(30), 116.8(9); C(12)–C(30)–C(21), 114.5(9); W(1)–P(1)–P(2)–W(2), –4.7(3); W(1)–P(1)–P(2)–C(7), 160.9(4); W(2)–P(2)–P(1)–C(1), –167.6(4); C(6)–C(21)–C(30)–C(12), –3(1).

E/Z photoisomerization^{12,13} was observed for both diphosphenes **7** and **8**. Upon prolonged irradiation, compound **6** appeared to be dimerized to a cyclotetraphosphane **9**. Although we have not been successful in isolation of *Z*-**6** during the photolysis of *E,E*-**7**, the *Z*-diphosphene was trapped by a complex formation with tungsten carbonyl.

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- 3**: Colorless needles, mp 207 – 208 °C (hexane); ¹H NMR (200 MHz, CDCl₃) δ = 1.22 (18H, s, *t*-Bu), 1.57 (18H, s, *t*-Bu), 3.17 (4H, s, CH₂), 6.93 (2H, d, ⁴J = 2.5 Hz, arom.), and 7.31 (2H, d, ⁴J = 2.5

- Hz, arom.); MS (70 eV) m/z (rel intensity) 566 ($M^+ + 4$; 3), 564 ($M^+ + 2$; 6), 562 (M^+ ; 3), 549 ($M^+ - \text{Me} + 2$; 2), 281 ($M^+ / 2$; 5), and 57 ($t\text{-Bu}^+$; 100). Found: C, 63.74; H, 7.93; Br, 28.08%. Calcd for $\text{C}_{30}\text{H}_{44}\text{Br}_2$: C, 63.83; H, 7.86; Br, 28.31%. 5: Colorless grains, mp 234–235 °C (decomp); ^1H NMR (600 MHz, CDCl_3) δ = 1.34 (18H, s, $p\text{-}t\text{-Bu}$), 1.61 (18H, d, $^5J_{\text{PH}} = 1.2$ Hz, $o\text{-}t\text{-Bu}$), 3.78 (4H, s, CH_2), 7.36 (2H, dd, $^4J_{\text{PH}} = 6.8$ Hz and $^4J_{\text{HH}} = 1.9$ Hz, arom.), and 7.75 (2H, d, $^4J_{\text{HH}} = 1.9$ Hz, arom.); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3) δ = 166.9; MS (70 eV) m/z (rel intensity) 608 ($M^+ + 2$; 5), 606 (M^+ ; 4), 571 ($M^+ - \text{Cl}$; 9), 535 ($M^+ - \text{Cl}_2 - 1$; 99), 504 ($M^+ - \text{PCl}_2 - 1$; 60), and 57 ($t\text{-Bu}^+$; 100). Found: m/z 606.1674. Calcd for $\text{C}_{30}\text{H}_{44}\text{Cl}_4\text{P}_2$: M, 606.1672. *E,E*-7: Orange solid, mp 186–187 °C; ^1H NMR (400 MHz, CDCl_3) δ = 1.32 (18H, s, $p\text{-}t\text{-Bu}$, Arra), 1.33 (18H, s, $p\text{-}t\text{-Bu}$, Ar), 1.35 (36H, s, $o\text{-}t\text{-Bu}$, Ar), 1.45 (18H, s, $o\text{-}t\text{-Bu}$, Arra), 3.18 (4H, s, CH_2), 7.14 (2H, d, $^4J_{\text{HH}} = 1.8$ Hz, arom., Arra), 7.39 (4H, s, $m\text{-Ar}$), and 7.44 (2H, d, $^4J_{\text{HH}} = 1.8$ Hz, arom., Arra); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3) δ = ABq, 476.7 and 515.9, $^1J_{\text{PP}} = 582.8$ Hz; UV (hexane) 280 (log ϵ 4.26), 327 (3.86), and 468 nm (2.68); MS (70 eV) m/z (rel intensity) 1017 ($M^+ - 1$; <1), 742 ($M^+ - \text{ArP}$; 1), 710 ($M^+ - \text{ArP}_2$; 4), 685 ($M^+ - \text{ArP} - \text{Bu}^+$; 33), 496 ($M^+ - \text{Ar}_2\text{P}_2$; 95), and 277 ($\text{ArP}^+ + 1$; 100). *E,Z*-7: ($\delta_{\text{P}} = \text{ABq}$, 519 and 487, $^1J_{\text{PP}} = 580$ Hz; $\delta_{\text{P}} = \text{ABq}$, 402 and 389, $^1J_{\text{PP}} = 555$ Hz). 9: Colorless, mp >300 °C; $\delta_{\text{P}} = -62$, $\delta_{\text{H}} = 1.35$ (36H, s, $t\text{-Bu}$), 1.38 (36H, s, $t\text{-Bu}$), 3.00 (4H, m, CHH-CHH), 5.60 (4H, m, CHH-CHH), 7.17 (4H, m, arom), 7.31 (4H, m, arom); MS (FAB) 931 ($M^+ - 1$). 10: Red crystals, mp 120 °C (decomp); $\delta_{\text{P}} = 332$, $J_{\text{PW}} = 145$ and 116 Hz; $\delta_{\text{H}} = 1.14$ (18H, s, $t\text{-Bu}$), 1.45 (18H, s, $t\text{-Bu}$), 3.14 (2H, m, CHH-CHH), 3.50 (2H, m, CHH-CHH), 6.74 (2H, m, arom), 7.22 (2H, m, arom). 11:¹⁵ $\delta_{\text{P}} = \text{ABq}$, 486 and 375 ($J_{\text{PW}} = 247$ Hz), $^1J_{\text{PP}} = 561.5$ Hz.
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