# Formation of a diphosphine: synthesis and molecular structure of bis(tetraphenylbutadienyl)diphosphine, $(Ph_4C_4)P–P(C_4Ph_4)$

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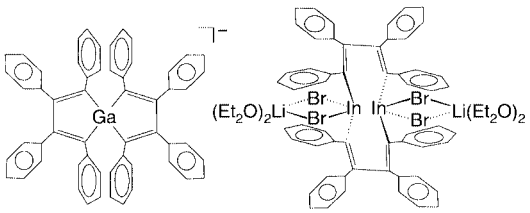
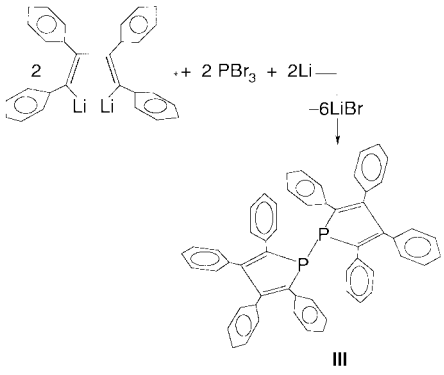
**Reaction of 1,4-dilithiotetraphenylbutadiene with phosphorus(III) bromide affords bis(tetraphenylbutadienyl)diphosphine, $(Ph_4C_4)P–P(C_4Ph_4)$, with a phosphorus–phosphorus bond length of 2.2051(11) Å.**

Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene, $(Bu^t_3C_6H_2)P{=}P(C_6H_2Bu^t_2)$,[1] the first compound shown to contain a formal phosphorus–phosphorus double bond [P–P 2.034(2) Å], was prepared by the magnesium metal reduction of $(Bu^t_3C_6H_2)PCl_2$. Indeed, alkali (or alkaline earth) metal reduction is one of three general routes to diphosphines (the other two being heating a phosphinous halide, $R_2PCl$, with a secondary phosphine or with an alkali metal phosphine),[2] a significant development in main group chemistry. Furthermore, as evidenced by subsequent studies concerning $(Bu^t_3C_6H_2)P{=}P(C_6H_2Bu^t_3)$,[3] the chemistry of diphosphenes and diphosphines continues to be of interest to both synthetic and computational chemists. Crucial in the stabilization of $(Bu^t_3C_6H_2)P{=}P(C_6H_2Bu^t_3)$ was the utilization of the sterically demanding 2,4,6-tri-*tert*-butylphenyl ligand. In a related vein, this laboratory has recently examined the organogroup 13 (III) chemistry of 1,4-dilithiotetraphenylbutadiene resulting in two interesting complexes: (a) a spirogallane anion,[4] $[(Ph_4C_4)Ga(C_4Ph_4)]^-$ **I**; and (b) an $In_2C_8$ ten-membered ring, $(Et_2O)_2Li(Br)_2In\{(C_4Ph_4)\}_2In(Br)_2Li(OEt_2)_2$ **II**.[5]




**I** **II**

Herein, we report the synthesis[6] and molecular structure[7] of bis(tetraphenylbutadienyl)diphosphine, $(Ph_4C_4)P–P(C_4Ph_4)$ **III**, readily isolated from reaction of 1,4-dilithiotetraphenylbutadiene,[8] prepared by the action of an excess of metallic lithium on diphenylacetylene, with phosphorus(III) bromide (Scheme 1). This compound, characterized by $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopy elemental analyses and single-crystal X-ray diffraction (Fig. 1), is significant as it represents an interestingly facile, if unexpected, one-pot route to a diphosphine.




**III**

**Scheme 1**

The past two decades have witnessed a number of studies concerning compounds containing phosphorus–phosphorus bonds.[9] Indeed, this laboratory has had an interest in the preparation of diphosphines having previously reported the synthesis and molecular structure of $[(Me_3Si)_2P\{Me_2Ga\}_2PMe]_2$,[10] isolated from reaction of $Me_3P–GaMe_3$ with $P(SiMe_3)_3$, having a P–P single bond length of 2.25(3) Å. Relative to diphosphenes it is important to note the previously reported σ-bonded pentamethylcyclopentadienyl-based diphosphene, bis(pentamethylcyclopentadienyl)diphosphene, $(\sigma\text{-}C_5Me_5)P{=}P(\sigma\text{-}C_5Me_5)$.[11] The phosphorus atoms in $(\sigma\text{-}C_5Me_5)P{=}P(\sigma\text{-}C_5Me_5)$ are two-coordinate (σ-bonding to one of the carbon atoms of the ring and to the other phosphorus atom) with a P–P double bond length of 2.031(3) Å.

A number of points regarding the structure and bonding in $(Ph_4C_4)P–P(C_4Ph_4)$ are relevant. As expected, the five-membered butadienyl rings are planar about the phosphorus atoms with the phenyl rings arranged in a propeller-like fashion. Indeed, the molecule resides in a *trans* configuration. The environment about the phosphorus atoms must be considered distorted pyramidal thereby precluding significant interaction of the phosphorus lone electron pairs with the conjugated system of the tetraphenylbutadienyl moieties. The P–C bond lengths are generally unremarkable. Clearly. the phosphorus–phosphorus bond of 2.2051(11) Å in $(Ph_4C_4)P–P(C_4Ph_4)$ must be considered a single bond. Moreover, the $^{31}P$ NMR resonance of $\delta$ −15.98 in $(Ph_4C_4)P–P(C_4Ph_4)$ is also consistent with a P–P single bond. For comparison, the $^{31}P$ resonance of $(\sigma\text{-}C_5Me_5)P{=}P(\sigma\text{-}C_5Me_5)$ was reported at $\delta$ 504 (121 MHz, $C_6D_6$)

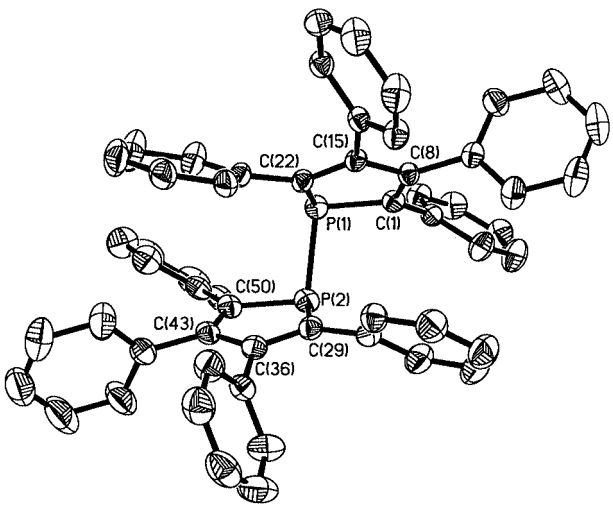



**Fig. 1** Molecular structure of $(Ph_4C_4)P–P(C_4Ph_4)$. Bond distances (Å) and angles (°): P(1)–C(22) 1.797(3), P(1)–C(1) 1.799(3), P(1)–P(2) 2.2051(11), P(2)–C(29) 1.796(3), P(2)–C(50) 1.799(3); C(22)–P(1)–C(1) 91.16(12), C(22)–P(1)–P(2) 108.13(9), C(1)–P(1)–P(2) 100.16(9), C(29)–P(2)–C(50) 91.26(14), C(29)–P(2)–P(1) 106.14(10), C(50)–P(2)–P(1) 99.92(10).

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while that for the [*trans*-{[Fe($CO_4$)]$_2$[PCH($SiMe_3$)$_2$]$_2$}] diphosphene was reported at $\delta$ 384.55 (external 85% $H_3PO_4$) [P–P 2.039(1) Å].[9b]

It is significant that the tetraphenylbutadienyl moiety continues to find utility in main group chemistry. It is noteworthy that the title compound bears some resemblance to the previously reported bis[1-(trimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclopentadienyl] compound isolated in 54% yield from the sonication of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene in the presence of three equivalents of metallic lithium.[12]

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## Notes and references


1 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4578.

2 D. E. C. Corbridge, *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, Elsevier, New York, 1985, p. 435.

3 A. H. Cowley, A. Decken, N. C. Norman, C. Krüger, F. Lutz, H. Jacobson and T. Ziegler, *J. Am. Chem. Soc.*, 1997, **119**, 3389.

4 J. Su, S. D. Goodwin, X.-W. Li and G. H. Robinson, *J. Am. Chem. Soc.*, 1998, **120**, 12 994.

5 B. C. Beck, J. Su, P. Wei, X.-W. Li and G. H. Robinson, *Organometallics*, 2000, **19**, 1214.

6 Inside a drybox (M Braun Labmaster 130) a reaction vessel was charged with phosphorus(III) bromide (1.08 g, 4 mmol), and diethyl ether (30 mL). Upon returning to the benchtop, 1,4-dilithiotetraphenylbutadiene, prepared by reaction of lithium (0.09 g, 12.96 mmol) and diphenylacetylene (1.74 g, 9.78 mmol) in diethyl ether, was slowly added to the reaction vessel at −78 °C over a period of 30 min *via* an addition funnel. The system was allowed to warm to room temperature and stir overnight. The solvent was removed *in vacuo*, and the solid was redissolved in hexane (40 mL). The resulting solution was filtered immediately and dried *in vacuo*. The solid was recrystallized in diethyl ether and resulted in yellow–orange crystals (0.56 g, 34% yield): mp 245–246 °C (decomp.). Anal. (E+R Microanalytical Labroatories, Parsipanny, NJ). Calc. (found) for $C_{59}H_{47}P_2$: C, 86.60 (86.51); H, 5.80 (5.76)%. $\delta_H$(300 MHz, 298 K, $CDCl_3$): 0.46 [q, 3H, $CH_3$ (hexane)], 0.84 [m, 4H, $CH_2$ (hexane)], 7.26–7.56 [m, 40H, CH (aromatic)] $\delta_C$(300 MHz, 298 K, $CDCl_3$): 14.01, 22.53, 31.47, 126.32, 127.09, 127.82, 129.60, 130.26, 136.52, 137.33, 143.85, 147.82, 151.75. $\delta_P$(300 MHz, 298 K, $CDCl_3$): −15.98.

7 X-Ray intensity data were measured at room temperature on a Bruker SMART™ CCD-based X-ray diffractometer system with graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct methods using the SHELXTL 5.1 system of computer programs. The non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in idealized positions with their coordinates and thermal parameters riding on the attached carbon atoms. *Crystallographic data*: monoclinic, space group *C*2/*c* (no. 15), $a$ = 28.092(4), $b$ = 13.6821(16), $c$ = 24.311(2) Å, $\beta$ = 98.078(5)°, $V$ = 9251.4(19) Å$^3$ and $Z$ = 8. The asymmetric unit contains one ($Ph_4C_4$)P–P($C_4Ph_4$) molecule and one-half hexane unit (situated about an inversion center). Refinement converged at $R1$ = 0.056 and $wR2$ = 0.132. CCDC 182/1625. See http://www.rsc.org/suppdata/cc/b0/b001257m/ for crystallographic files in .cif format.

8 A. Orechoff, *Chem. Ber.*, 1914, **47**, 89; W. Schlenk and E. Bergmann, *Annales*, 1928, **463**, 71; E. Bergmann and O. Zwecker, *Annales*, 1931, **487**, 155; E. Bergmann and W. Schreiber, *Annales*, 1933, **500**, 118; L. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, 1941, **63**, 1184.

9 (*a*) J. E. Richman, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.*, 1980, **102**, 3955; (*b*) K. M. Flynn, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 2085: (*c*) D. C. Pestana and P. P. Power, *J. Am. Chem. Soc.*, 1989, **111**, 6887; (*d*) M. Drieß, P. Frankhauser, H. Pritzkow and W. Siebert, *Chem. Ber.*, 1991, **124**, 1497.

10 J. A. Burns, W. T. Pennington and G. H. Robinson, *Organometallics*, 1995, **14**, 1533.

11 P. Jutzi, U. Meyer, B. Krebs and M. Dartmann, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 919.

12 J.-H. Hong, P. Boudjouk and S. Castellino, *Organometallics*, 1994, **13**, 3387.