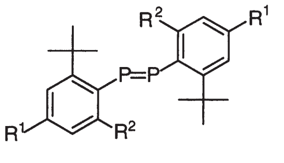
Preparation and Properties of Sterically Protected Diphosphene and Fluorenylidenephosphine Bearing the 2,6-Di-*tert*-butyl-4-methoxyphenyl Group

Kozo Toyota, Subaru Kawasaki, Akitake Nakamura, and Masaaki Yoshifuji*
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578

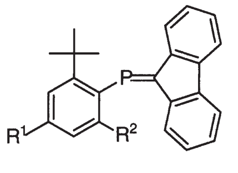
(Received January 30, 2003; CL-030091)

A new bulky bromobenzene, 2-bromo-1,3-di-*tert*-butyl-5-methoxybenzene, was prepared and utilized to preparations of the corresponding diphosphene and fluorenylidenephosphine including low-coordinate phosphorus atom(s). An electronic perturbation of the *p*-methoxy group in the system was indicated by UV–vis spectra and ^{31}P NMR chemical shifts.

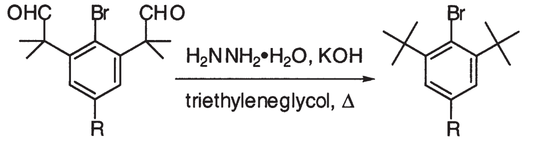
Intramolecular interactions between a reactive site and the neighboring functional group are of current interest.[1] Sterically protected diphosphenes include an essentially reactive –P=P– bond in the molecule and they are kinetically stabilized by bulky groups such as the 2,4,6-tri-*tert*-butylphenyl group.[2] We have studied modification of the bulky aryl substituents at the *o*-position(s) and prepared 1,2-bis[2,4-di-*tert*-butyl-6-(dimethylamino)phenyl]diphosphene (**1b**) as an *o*-amino analogue of **1a**.[3] It should be noted that an attempted preparation of 1,2-bis(2,4-di-*tert*-butyl-6-methoxyphenyl)diphosphene (**1c**) has been unsuccessful.[4] In contrast, studies concerning the effect of *p*-substituent(s) in diaryldiphosphenes have been limited.[5] Although we have reported preparation of diphosphenes lacking the *p*-*tert*-butyl groups, i.e., 1,2-bis(2,6-di-*tert*-butylphenyl)diphosphene (**1d**),[6] the effect of introduction of an electron-donating or an electron-withdrawing substituent at the *p*-position of the 2,6-di-*tert*-butylphenyl group has remained unclear. We report here preparation and properties of *p*-methoxy substituted diphosphene **1e**, as well as fluorenylidenephosphines **2d** and **2e**.



1a: $R^1 = R^2 = t\text{-Bu}$
b: $R^1 = t\text{-Bu}$, $R^2 = NMe_2$
c: $R^1 = t\text{-Bu}$, $R^2 = OMe$
d: $R^1 = H$, $R^2 = t\text{-Bu}$
e: $R^1 = OMe$, $R^2 = t\text{-Bu}$



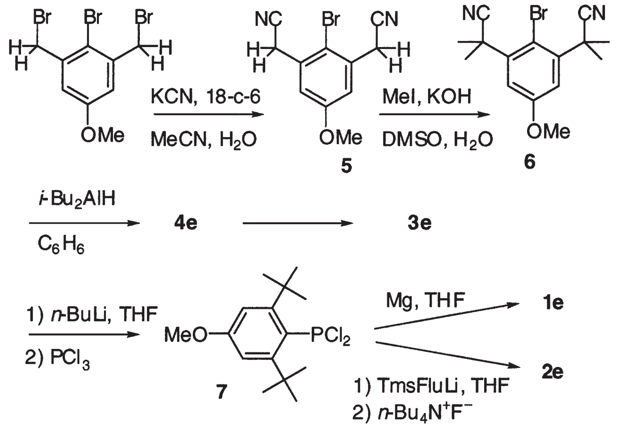
2a: $R^1 = R^2 = t\text{-Bu}$
d: $R^1 = H$, $R^2 = t\text{-Bu}$
e: $R^1 = OMe$, $R^2 = t\text{-Bu}$



4d: R=H; **e**: R=OMe **3d**: R=H; **e**: R=OMe

First, we tried to prepare a bulky bromobenzene **3d**. Although the compound **3d** was first prepared by Rundel, starting from 2,4,6-tri-*tert*-butylaniline,[7] the reported yield was not good.[6,7] Thus, we have sought an alternative synthetic route and found that the Wolff-Kishner (the Huang-Minlon method) reduction[8] of **4d**[9] afforded **3d** in good yield (70%).

Then we applied this methodology to the preparation of **3e** as follows: 2-bromo-1,3-bis(bromomethyl)-5-methoxybenzene[10] was allowed to react with KCN in acetonitrile (containing ca. 10% of water) in the presence of 18-crown-6 at room temperature for 24 h to give **5** in 66% yield.[11] Methylation of **5** to **6** (quant.) followed by treatment with diisobutylaluminum hydride gave **4e** (96% yield), which was then reduced to **3e** (48% yield)[11] by the Huang-Minlon method. Lithiation of **3e** with butyllithium followed by reaction with PCl_3 gave **7** [^{31}P NMR (THF-C_6D_6) $\delta_P = 153.3$], which was then converted to **1e** in 12% isolated yield.[12] Reaction of **7** with 9-(trimethylsilyl)-9-fluorenyllithium followed by treatment with $n\text{-}Bu_4N^+F^-$ gave **2e**[12] (38% yield). Compound **2d** was prepared from **3d** by a method similar to that for **2e** (86% yield).[12]



18-c-6 = 18-crown-6; TmsFluLi = 9-(trimethylsilyl)-9-fluorenyllithium

Table 1 shows ^{31}P NMR chemical shifts and UV–vis data of **1a,d,e** and **2a,d,e**. As for the ^{31}P NMR chemical shift, electron-donating substituent in **1a,e** and **2a,e** causes a shift to a lower field, compared to that of **1d** and **2d**, respectively. The order of the δ_P values is **d**<**a**<**e**, for both diphosphene and fluorenylidenephosphine series. In the case of UV–vis spectra of **1a,d,e**, the *p*-substitution causes red shifts of absorption of the longest λ_{max} attributable to $n \rightarrow \pi^*$ transition (again, the order is **d**<**a**<**e**). In contrast, *p*-substitution effect on the second λ_{max} ($\pi \rightarrow \pi^*$ transition) is small. These facts may indicate that the *p*-methoxy group affects the electronic states of the phosphorus lone pair, although the effect on the –P=P– π system is small, probably because the π-conjugation between the aromatic rings and the phosphorus double bonds is restricted, due to steric hindrance that prevents coplanar conformation.[2,13]

Structure of **1e** was unambiguously determined by X-ray crystallography.[16] Figure 1 shows a molecular structure of **1e**. Although the P–C$_{ipso}$ bond lengths for **1e** [1.860(4) Å for P(1)–C(1) and 1.869(4) Å for P(2)–C(7)] are very close to those

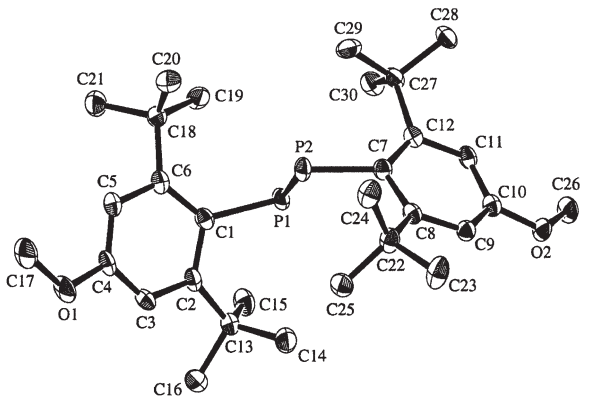


Figure 1. Molecular structure of **1e**, showing the atomic labeling scheme with thermal ellipsoids (50% probability). Hydrogen atoms are omitted for clarity. Some selected bond lengths (Å) and angles (°): P(1)–P(2), 2.043(1); P(1)–C(1), 1.860(4); P(2)–C(7), 1.869(4); O(1)–C(4), 1.372(4); O(2)–C(10), 1.370(4); P(1)–P(2)–C(7), 98.7(1); P(2)–P(1)–C(1), 100.5(1).

Table 1. ^{31}P NMR and UV-vis data of compounds **1** and **2**

Compd.	δ_P[a]	λ/nm (log ε)			
1a	490.0[b]	284 (4.19)[c,d]	340 (3.89)	460 (3.13)	
1d	488.7[e]	290 (4.03)[c,e]	340 (3.85)	450 (3.00)	
1e	495.9	291 (4.21)[c]	346 (3.75)	477 (3.12)	
2a	256.5[f]	238 (4.48)[g]	266 (4.30)	275 (4.32)	365 (4.05)
2d	254.8	237 (4.55)[g]	266 (4.40)	275 (4.45)	362 (4.25)
2e	258.0	239 (4.61)[g]	266 (4.42)	275 (4.46)	369 (4.30)

[a]Measured in $CDCl_3$. [b]Data taken from Ref. 14. [c]Measured in CH_2Cl_2. [d]Data taken from Ref. 2a. [e]Data taken from Ref. 6. [f]Data taken from Ref. 1b, see also, Ref. 15. [g]Measured in hexane.

for **1a** [1.862(2) Å],[2a] the P=P bond length for **1e** [2.043(1) Å] is slightly longer than that for **1a** [2.034(2) Å]. The interplanar angles between the average plane [P(1), P(2), C(1), C(7)] and the aromatic rings [C(1)–C(6) and C(7)–C(12)] are 70.18(10) and 108.08(10)°, respectively, whereas the corresponding angle is 63.9 ° in **1a**. The interplanar angle between the two aromatic rings of **1e** is 70.7(1)°. The dihedral angle C(1)–P(1)–P(2)–C(7) for **1e** [165.0(2)°] is smaller than that for **1a** [172.2(1)°], which means that the deviation from the planarity of the –P=P– moiety is larger in **1e** than in **1a** in the crystal.

In summary, we have developed a new bulky substituent bearing a *p*-methoxy group. Some low-coordinated phosphorus compounds bearing the substituent were prepared and the effects of the *p*-substituent were evaluated. The method described here is promising for preparations of various *p*-functionalized bulky bromobenzenes. Studies on the reactivities of **1e** and **2e** are now in progress.

This work was supported in part by the Grants-in-Aid for Scientific Research (Nos. 13304049, 14044012, and 13640522) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 a) J. G. Verkade, *Acc. Chem. Res.*, **26**, 483 (1993). b) K. Toyota, S. Kawasaki, and M. Yoshifuji, *Tetrahedron Lett.*, **43**, 7953 (2002).

2 a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981); M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **104**, 6167 (1982). b) M. Yoshifuji, *J. Organomet. Chem.*, **611**, 210 (2000).

3 M. Yoshifuji, M. Hirano, and K. Toyota, *Tetrahedron Lett.*, **34**, 1043 (1993).

4 M. Yoshifuji, D.-L. An, K. Toyota, and M. Yasunami, *Chem. Lett.*, **1993**, 2069.

5 *p*-Phenylene-bridged bis(diphosphene) derivative has recently been reported. See, S. Shah, T. Concolino, A. L. Rheingold, and J. D. Protasiewicz, *Inorg. Chem.*, **39**, 3860 (2000).

6 M. Yoshifuji, T. Niitsu, D. Shiomi, and N. Inamoto, *Tetrahedron Lett.*, **30**, 5433 (1989).

7 W. Rundel, *Chem. Ber.*, **101**, 2956 (1968).

8 K. Toyota, Y. Matsushita, N. Shinohara, and M. Yoshifuji, *Heteroat. Chem.*, **12**, 418 (2001).

9 K. Toyota, A. Nakamura, and M. Yoshifuji, *Chem. Commun.*, **2002**, 3012.

10 L. A. van de Kuil, H. Luitjes, D. M. Grove, J. W. Zwikker, J. G. M. van der Linden, A. M. Roelofsen, L. W. Jenneskens, W. Drenth, and G. van Koten, *Organometallics*, **13**, 468 (1994).

11 **3e**: mp 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.63$ (18H, s, *t*-Bu), 3.85 (3H, s, OMe), 7.02 (2H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 31.2$ (C$\underline{Me}_3$), 38.7 ($\underline{C}$Me$_3$), 55.5 (OMe), 112.7, 115.9, 151.0, 157.9; MS (70 eV) m/z 300 (M^++2; 100), 298 (M^+; 100), 285 (M^+–Me+2; 33), 283 (M^+–Me; 33). Found: m/z 298.0934. Calcd for $C_{15}H_{23}BrO$: M, 298.0932. **4e**: mp 98–100 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.54$ (12H, s, CMe$_2$), 3.88 (3H, s, OMe), 6.99 (2H, s), 9.78 (2H, s, CHO); ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 24.3$ (C$\underline{Me}_2$), 53.2 ($\underline{C}$Me$_2$), 55.9 (OMe), 114.5, 115.7, 145.9, 159.6, 203.0 (CHO); MS m/z 328 (M^++2; 6), 326 (M^+; 6), 247 (M^+–Br; 100). Found: m/z 326.0521. Calcd for $C_{15}H_{19}BrO_3$: M, 326.0518. **5**: mp 155–157 °C; ^{1}H NMR ($CDCl_3$) $\delta = 3.86$ (4H, s, CH_2CN), 3.88 (3H, s, OMe), 7.10 (2H, s); ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 26.1$ (CH_2), 56.2 (OMe), 115.2, 115.9, 116.9, 132.7, 159.8; MS m/z 266 (M^++2; 98) 264 (M^+; 100). Found: m/z 263.9905. Calcd for $C_{11}H_9BrN_2O$: M, 263.9898. **6**: mp 149–151 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.95$ (12H, s, CMe$_2$CN), 3.87 (3H, s, OMe), 7.05 (2H, s); ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 28.7$ (C$\underline{Me}_2$), 38.6 ($\underline{C}$Me$_2$), 56.0 (OMe), 113.6, 114.8, 123.7, 142.2, 159.2; MS m/z 322 (M^++2; 99) 320 (M^+; 100). Found: m/z 320.0520. Calcd for $C_{15}H_{17}BrN_2O$: M, 320.0524.

12 **1e**: Orange prisms, mp 165–169 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.41$ (36H, s, *t*-Bu), 3.56 (6H, s, OMe), and 7.14 (4H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 55.4$ (OMe); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) $\delta = 498.8$; MS (70 eV) m/z 500 (M^+; 16) and 249 (ArP^+–1; 100). Found: m/z 500.3000. Calcd for $C_{30}H_{46}O_2P_2$: M, 500.2973. **2d**: Yellow needles, mp 162–164 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.46$ (18H, s, *t*-Bu), 5.29 (1H), 6.78 (1H), 7.17 (1H), 7.29–7.37 (2H), 7.45–7.59 (4H), 7.64 (1H), and 8.28 (1H); ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 170.3$ (d, $^{1}J_{PC} = 42.2$ Hz, P=$\underline{C}$); ^{31}P{^{1}H} NMR (C_6D_6) $\delta = 253.5$; MS m/z 384 (M^+; 27) and 219 (ArP^+–1; 100). Found: m/z 384.2007. Calcd for $C_{27}H_{29}OP$: M, 384.2007. **2e**: Yellow prisms, mp 205–207 °C (dec.); ^{1}H NMR ($CDCl_3$) $\delta = 1.44$ (18H, s, *t*-Bu), 3.96 (3H, s, OMe), 5.56 (1H), 6.84 (1H), 7.14 (2H), 7.18 (1H), 7.28–7.37 (2H), 7.57 (1H), 7.64 (1H), and 8.27 (1H); ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 171.2$ (d, $^{1}J_{PC} = 43.2$ Hz, P=$\underline{C}$); ^{31}P{^{1}H} NMR (C_6D_6) $\delta = 257.2$; MS m/z 414 (M^+; 18), 249 (ArP^+–1; 100), and 165 (Flu^++1; 33). Found: m/z 414.2104. Calcd for $C_{28}H_{31}OP$: M, 414.2113.

13 R. Gleiter, G. Friedrich, M. Yoshifuji, K. Shibayama, and N. Inamoto, *Chem. Lett.*, **1984**, 313.

14 D.-L. An, K. Toyota, M. Yasunami, and M. Yoshifuji, *J. Organomet. Chem.*, **508**, 7 (1996).

15 V. D. Romanenko, A. V. Ruban, M. I. Povolotskii, L. K. Polyachenko, and L. N. Markovskii, *Zh. Obshch. Khim.*, **56**, 1186 (1986).

16 Recrystallized from CH_2Cl_2–hexane, measured at 153 K. $C_{30}H_{46}O_2P_2$, $M = 500.64$. Monoclinic, space group $P2_1/n$ (#14), $a = 10.181(7)$, $b = 19.299(4)$, $c = 15.413(3)$ Å, $\beta = 104.75(3)$ °, $V = 2928(2)$ Å^3, $Z = 4$, $Dc = 1.135$ g cm^{-3}, μ (Mo Kα) = 1.72 cm^{-1}. 3955 Unique reflections with $2\theta \leq 50.0$ °. Of these, 3683 with $I > 2.0\,\sigma(I)$ were used for R_1 calculation. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. $R_1 = 0.073$, $R = 0.134$, $R_w = 0.178$. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-202408).