JOC*Article*

Preparation and Properties of Phosphaethynes Bearing Bulky Aryl Groups with Electron-Donating Substituents at the Para Position

Kozo Toyota, Subaru Kawasaki, and Masaaki Yoshifuji*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

yoshifj@mail.tains.tohoku.ac.jp

Received March 16, 2004

Phosphaethynes bearing a 2,6-di-*tert*-butyl-4-(dimethylamino)phenyl, 2,6-di-*tert*-butyl-4-methoxyphenyl, or 2,6-di-*tert*-butylphenyl group were prepared. A ^{31}P NMR spectroscopic investigation of the chemical shifts indicated that electron-donating groups at the para position cause shifts to a higher field. Bathochromic shifts caused by the electron-donating groups were apparently observed in UV−vis spectra. The structure of 2-[2,6-di-*tert*-butyl-4-(dimethylamino)phenyl]-1-phosphaethyne was analyzed by X-ray crystallography.

Introduction

Understanding and controlling the multiple bonds between the heavier main group elements is one of the most attractive and important subjects in modern main-group chemistry.[1] In general, such multiple bonds are highly reactive but several methodologies for stabilization of such reactive bonds have been developed. Thermodynamic stabilization by electronic perturbation has been used in studies of multiple bonds between carbon and heavier heteroatoms,[2] and more recently, intramolecular donor-stabilization[3] and kinetic stabilization[4] have been effectively applied to multiple bonds between the heavier heteroatoms. In this context, the systematic comparison of properties of electronically perturbed multiple bonds with those of kinetically stabilized, but less electronically perturbed multiple bonds is now a subject of interest in heteroatom chemistry.

We and others have studied properties of low-coordinated phosphorus compounds[5] such as diphosphenes,[4b,c] phosphaethenes,[2,4a,6] and phosphaethynes,[7,8] as well as those in conjugation or cumulative systems such as phosphapolyenes[9] or phosphaallenes,[10] respectively. Research on conjugated systems containing phosphorus−carbon *double* bonds has been developed both experimentally and theoretically; however, conjugated phosphorus−carbon *triple* bonds have scarcely been studied. Since the

(1) For recent reviews, (a) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (b) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (c) Grützmacher, H.; Fässler, T. F. *Chem. Eur. J.* **2000**, 2317. (d) Jutzi, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3797. (e) Escudié, J.; Ranaivonjatovo, H.; Rigon, L. *Chem. Rev.* **2000**, *100*, 3639. (f) Weber, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 563. (g) Weidenbruch, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2222. (h) Power, P. P. *Chem. Commun.* **2003**, 2091.

(2) (a) Dimroth, K.; Hoffmann, P. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 384. (b) Märkl, G. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 846. (c) Becker, G. *Z. Anorg. Allg. Chem.* **1976**, *423*, 242.

(3) For example: (a) Arya, P.; Boyer, J.; Carré, F.; Corriu, R. J. P.; Lanneau, G.; Lapasset, J.; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016. (b) Schmidt, H.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G.; Schoeller, W. W.; Jutzi, P. *Organometallics* **1998**, *17*, 2149. (c) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G. *Organometallics* **1999**, *18*, 4778. (d) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammler, A.; Stammler, H.-G. *Organometallics* **2001**, *20*, 42. (e) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483. (f) Yoshifuji, M.; Hirano, M.; Toyota, K. *Tetrahedron Lett.* **1993**, *34*, 1043. (g) Yoshifuji, M.; An, D.-L.; Toyota, K.; Yasunami, M. *Chem. Lett.* **1993**, 2069. (h) Yoshifuji, M.; Sangu, S.; Kamijo, K.; Toyota, K. *Chem. Ber.* **1996**, *129*, 1049.

(4) For example: (a) Klebach, Th. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4886. (b) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587. (c) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1982**, *104*, 6167. (d) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. (e) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *277*, 78. (f) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785.

(5) (a) Regitz, M.; Scherer, O. J. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Georg Thieme Verlag: Stuttgart, Germany, 1990, and references therein. (b) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus*: *The Carbon Copy*; John Wiley: Chichester, UK, 1998. (c) Yoshifuji, M. *J. Organomet. Chem.* **2000**, *611*, 210.

(6) For example: (a) Issleib, K.; Schmidt, H.; Wirkner, C. *Z. Anorg. Allg. Chem.* **1982**, *488*, 75. (b) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 1727.

(7) For example: (a) Gier, T. E. *J. Am. Chem. Soc.* **1961**, *83*, 1769. (b) Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1978**, *100*, 446. (c) Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *Chem. Phys. Lett.* **1976**, *42*, 460. (d) Becker, G.; Gresser, G.; Uhl, W. *Z. Naturforsch. B* **1981**, *36*, 16. (e) Allspach, T.; Regitz, M.; Becker, G.; Becker, W. *Synthesis* **1986**, 31. (f) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159. (g) Ohno, K.; Kroto, H. W.; Nixon, J. F. *J. Mol. Spectrosc.* **1981**, *90*, 507. (h) Kroto, H. W.; Nixon, J. F.; Ohno, K. *J. Mol. Spectrosc.* **1981**, *90*, 512. (i) Cooper, T. A.; Kroto, H. W.; Nixon, J. F.; Ohashi, O. *J. Chem. Soc., Chem. Commun.* **1980**, 333. (j) Markovskii, L. N.; Koidan, G. N.; Marchenko, A. P.; Romanenko, V. D.; Povolotskii, M. I.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1989**, *59*, 2133. (k) Grobe, J.; Le Van, D.; Lüth, B.; Hegemann, M. *Chem. Ber.* **1990**, *123*, 2317. (l) Grobe, J.; Le Van, D.; Pohlmeyer, T.; Immel, F.; Pucknat, H.; Krebs, B.; Kuchinke, J.; Läge, M. *Tetrahedron* **2000**, *56*, 27 and references therein.

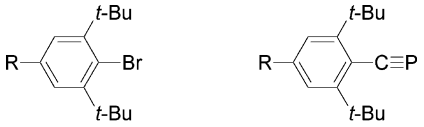
(8) (a) Appel, R.; Maier, G.; Reisenauer, H. P.; Westerhaus, A. *Angew. Chem., Int Ed Engl.* **1981**, *20*, 197. (b) Mack, A.; Pierron, E.; Allspach, T.; Bergsträsser, U.; Regitz, M. *Synthesis* **1998**, 1305. (c) Märkl, G.; Sejpka, H. *Tetrahedron Lett.* **1986**, *27*, 171. (d) Yoshifuji, M.; Kawanami, H.; Kawai, Y.; Toyota, K.; Yasunami, M.; Niitsu, T.; Inamoto, N. *Chem. Lett.* **1992**, 1053. (e) Fleischer, U.; Kutzelnigg, W. *Phosphorus, Sulfur, Silicon* **1993**, *77*, 105.

(9) For example: (a) Appel, R.; Hünerbein, J.; Siabalis, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 779. (b) Ito, S.; Toyota, K.; Yoshifuji, M. *Chem. Lett.* **1995**, 747. (c) Appel, R.; Winkhaus, V.; Knoch, F. *Chem. Ber.* **1987**, *120*, 243. (d) Toyota, K.; Tashiro, K.; Yoshifuji, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1163.

10.1021/jo049571q CCC: $27.50
Published on Web 07/01/2004

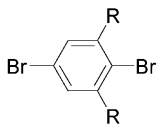
first generation of parent phosphaethyne by Gier,[7a] generation or preparation of several carbon- or heteroatom-substituted phosphaethyne derivatives such as fluoro-,[7b] alkyl-,[7c−e] vinyl-,[7f] ethynyl-,[7g] cyano-,[7h] trimethylsilyl-,[7i] or diisopropylamino-substituted phosphaethynes[7k,l] have been reported. In contrast to the alkylphosphaethynes, studies on aryl-substituted phosphaethynes[8] have been limited, despite the expectation that aryl moieties may interact more effectively than alkyl groups do and that introduction of functional groups is easier than that of the alkyl groups. To the best of our knowledge, the preparations of only four metal-free arylphosphaethynes (i.e., phenyl-,[8a] mesityl-,[8b] 2,4,6-tri-*tert*-butylphenyl-,[8c] and 2,4,6-tri-*tert*-pentylphenyl-substituted[8d] phosphaethynes) have been reported so far. Although a theoretical calculation concerning (2,6-dimethylphenyl)phosphaethyne was reported,[8e] this phosphaethyne has not been experimentally realized.

It should be noted that substituents on the aromatic rings are limited to three simple alkyl groups (i.e., methyl, *tert*-butyl, and *tert*-pentyl) in the reported arylphosphaethynes, and no heteroatom-containing group has been introduced as a substituent into the aromatic ring, probably because of relatively high reactivities of arylphosphaethynes. However, sterically hindered aryl substituents containing some functional groups are expected to afford new arylphosphaethynes as stable compounds and will help to gain insight into the structure−properties relationship of arylphosphaethynes. It may also help to develop applications of the electronically perturbed phosphaethynes and/or their metal complexes in the field of materials science and as catalysts in synthetic organic chemistry. For this purpose, we designed new para-functionalized bulky aryl substituents simultaneously containing *tert*-butyl groups at the ortho positions: We report here the preparation and properties of kinetically stabilized and electronically perturbed phosphaethynes **2b**,**c** bearing para-functionalized bulky aryl groups as well as para-nonsubstituted congener **2a**. These new arylphosphaethynes may help in understanding the nature of the interaction between the P−C triple bond and the aromatic π-system.



1a: R = H; **b**: R = OMe;
c: R = NMe_2; **d**: R = *t*-Bu;
e: R = Br; **f**: R = N=CPh_2;
g: R = NH_2

2a: R = H;
b: R = OMe;
c: R = NMe_2;
d: R = *t*-Bu



3: R = Me
4: R = CH_2Br
5: R = CH_2CN
6: R = CMe_2CN
7: R = CMe_2CHO

Results and Discussion

Preparation of Bulky Bromobenzenes. The starting bulky bromobenzenes, 2-bromo-1,3-di-*tert*-butylbenzene (**1a**) and 2-bromo-1,3-di-*tert*-butyl-5-methoxybenzene (**1b**), were prepared as described in a previous report.[11a] The method for the preparation of **1c** by Rundel[12a] starting from 4-nitro-2,6-di-*tert*-butylaniline was found to be rather inefficient due to formation of byproducts and an elaborate separation process.[12b] Therefore we prepared **1c** as follows: 3,5-xylidine was brominated with NBS in acetonitrile,[13] to give 4-bromo-3,5-xylidine[14] (98% yield), which was then converted to 2,5-dibromo-1,3-dimethylbenzene (**3**)[15] by Sandmeyer reaction with use of CuBr/HBr (38% yield). Bromination of **3** with NBS in CCl_4 gave compound **4** (55% yield), which was then cyanated with KCN to form **5** (90% yield). Treatment of **5** with MeI and KOH in DMSO gave **6** in 87% yield. Reduction of **6** to the corresponding dialdehyde **7** by DIBAL, followed by Wolff−Kishner reduction (the Huang−Minlon method) afforded 3,5-dibromo-1,3-di-*tert*-butylbenzene (**1e**) (20% yield based on **6**). Regioselective amination of **1e** with benzophenone imine in the presence of palladium catalyst[16] afforded **1f** (97% yield), and **1f** was then hydrolyzed to **1g**[12] with hydrochloric acid (57% yield). *N*-Methylation of **1g** by treatment with Formalin and $NaBH_4$ gave the bromobenzene **1c** in 84% yield.

Although we could obtain compound **1c** as described above via **1e** (as mentioned above, **1e** was prepared from commercially available 3,5-xylidine in 7 steps in 3% overall yield), this route has the following disadvantage: Workup of the Sandmeyer reaction providing **3** was tedious due to the separation of the copper byproducts from **3** and the reproducibility was unsatisfactory (yields were ca. 20−40%). Alternatively, we found that the direct bromination of **1a** (prepared from commercially available 2-bromo-*m*-xylene) in trimethyl phosphate also gave **1e** as a sole product in 63% yield (6 steps from the starting 2-bromo-*m*-xylene in 12% overall yield) without formation of the possible byproduct 2,4-dibromo-1,3-di-*tert*-butylbenzene (Scheme 1). It should be noted that an attempted direct bromination of 2-bromo-*m*-xylene under similar conditions resulted in the formation of a mixture of *m*- and *p*-dibromo derivatives, probably because the steric hindrance of the *tert*-butyl group plays an important role in the regioselective bromination of **1a**. Compared with Rundel's preparative method[12a] for **1c** (3 steps from 4-nitro-2,6-di-*tert*-butylaniline), our present route requires 9 steps from 2-bromo-*m*-xylene to **1c** via **1e**; however, our method is reliable and the workup is easy for each step, making large scale preparation possible (1.7 g of **1c** was prepared from 2-bromo-*m*-xylene within 2 weeks).

(10) (a) Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809. (b) Yoshifuji, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1984**, 689. (c) Karsch, H. H.; Köhler, F. H.; Reisacher, H.-U. *Tetrahedron Lett.* **1984**, *25*, 3687. (d) Appel, R.; Fölling, P.; Josten, B.; Siray, M.; Winkhaus, V.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 619. (e) Märkl, G.; Sejpka, H.; Dietl, S.; Nuber, B.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1003. (f) Märkl, G.; Kreitmeier, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1360.

(11) (a) Toyota, K.; Kawasaki, S.; Nakamura, A.; Yoshifuji, M. *Chem. Lett.* **2003**, *32*, 430. See also: (b) Toyota, K.; Nakamura, A.; Yoshifuji, M. *Chem. Commun.* **2002**, 3012. (c) Toyota, K.; Matsushita, Y.; Shinohara, N.; Yoshifuji, M. *Heteroat. Chem.* **2001**, *12*, 418.

(12) (a) Rundel, W. *Chem. Ber.* **1968**, *101*, 2956. See also: (b) Yoshifuji, M.; Niitsu, T.; Shiomi, D.; Inamoto, N. *Tetrahedron Lett.* **1989**, *30*, 5433.

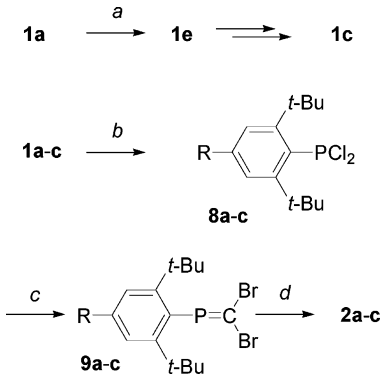
(13) Fox, G. J.; Hepworth, J. D.; Paskins, K. N. *Org. Synth.* **1976**, *55*, 20.

(14) Courtin, A.; von Tobel, H.-R. *Helv. Chim. Acta* **1977**, *60*, 1994.

(15) Blanksma, J. J. *Recl. Trav. Chim. Pays-Bas* **1906**, *25*, 165.

(16) Mann, G.; Hartwig, J. F.; Driver, M. S.; Fernández-Rivas, C. *J. Am. Chem. Soc.* **1998**, *120*, 827.

SCHEME 1[a]



[a] Reagents and conditions: (a) Br_2, $P(O)(OMe)_3$, 63% yield; (b) *n*-BuLi, THF, then PCl_3; (c) LDA, $CHBr_3$, THF [**9a**: 47% yield based on **1a**; **9b**: 64% yield based on **1b**; **9c**: not isolated]; (d) $NiBr_2(PPh_3)_2$, PPh_3, Zn, *n*-$Bu_4N^+I^-$, THF [**2a**: 24% yield based on **9a**; **2b**: 30% yield based on **9b**; **2c**: 32% yield based on **1c**].

TABLE 1. ^{31}P NMR (162 MHz), ^{13}C NMR (100 MHz), and UV−Vis Data for 2a−d

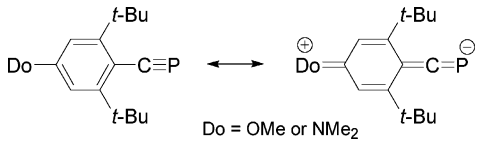
compd	R	δ_P[a]	$\delta_C(C{\equiv}P)$[b] ($^1J_{PC}$/Hz)	λ_{max}/nm (log ϵ)[c]
2a	H	37.2	168.3 (54.0)	315 (4.03), 330 (3.94)
2b	OMe	32.4	168.9 (52.4)	330 (4.22)
2c	NMe_2	32.1	171.4 (49.8)	377 (4.50)
2d[d]	*t*-Bu	34.4	168.7 (53.2)	320 (4.17), 334 (4.09)

[a] In $CDCl_3$, relative to external 85% H_3PO_4. [b] In $CDCl_3$. [c] In CH_2Cl_2. [d] Data taken from ref 8c (^{31}P NMR, 101.25 MHz; ^{13}C NMR, 62.9 MHz).

Preparation and Properties of Phosphaethynes. Having obtained the bromobenzenes **1a**−**c**, we then prepared phosphaethynes **2a**−**c** as follows (Scheme 1): Bromobenzenes **1a**−**c** were converted to the corresponding phosphonous dichlorides **8a**,[12b] **8b**,[11] and **8c** [**8c**: not isolated, $^{31}P\{^1H\}$ NMR (162 MHz, THF−C_6D_6) δ_P 155.7], which were allowed to react with bromoform and LDA[17] to give dibromomethylenephosphines **9a**−**c** [**9a**: δ_P ($CDCl_3$) 269.2; **9b**: δ_P ($CDCl_3$) 270.8; **9c** (not isolated, due to its instability in air): δ_P (C_6D_6) 276.3]. Dehalogenation reactions of **9a**−**c** via 1,2-shift[18] with $NiBr_2(PPh_3)_2$ as catalyst[18a] gave phosphaethynes **2a**−**c**.

Table 1 shows selected spectral data for **2a**−**c**, together with those for **2d**.[8c] ^{31}P NMR signals of **2** shift to a lower field [order of the δ_P values: **c** (NMe_2) < **b** (OMe) < **d** (*t*-Bu) < **a** (H), larger positive values correspond to the lower field] when the electron donating ability of the para-functional group decreases.[19] The values of chemical shifts (δ_C) of the sp carbons in ^{13}C NMR spectra are very close among the four phosphaethynes. Differences in the values of spin−spin coupling constants ($^1J_{PC}$) are also small; however, they become slightly smaller as the electron-donating ability of the para-functional groups increases (i.e., again the order is **c** < **b** < **d** < **a**). This tendency in $^1J_{PC}$ may indicate that the PC bond order decreases, in electron donating group-substituted arylphosphaethynes such as **2b**,**c**, by contribution of the resonance shown in Scheme 2.

SCHEME 2



These tendencies in the δ_P and $^1J_{PC}$ values are consistent with the cases of phosphaethynes HC≡P, *t*-BuC≡P, and *i*-$Pr_2NC{\equiv}P$ (it should be noted that experimental data for methoxy- or dimethylamino-substituted phosphaethynes are not available because these compounds have not been prepared). As for the ^{31}P NMR chemical shift, the order of the δ_P values is *i*-$Pr_2NC{\equiv}P$ (δ_P −99.6) < *t*-BuC≡P (δ_P −69.2) < HC≡P (δ_P −32).[7d,k] The order of the $^1J_{PC}$ values is also *i*-$Pr_2NC{\equiv}P$ (14.7 Hz) < *t*-BuC≡P (38.5 Hz) < HC≡P (56.0 Hz),[7d,k] which matches the order in the arylphosphaethynes (**2c** < **2b** < **2d** < **2a**), although the differences between the values are smaller in the case of **2**.

Concerning the stabilities or reactivities of the phosphaethynes, *i*-$Pr_2NC{\equiv}P$ slowly decomposes above −20 °C, while *t*-BuC≡P is stable at room temperature, under inert atmosphere. In this case, however, steric hindrance around the triple bond seems to have a large effect on the stability, and indeed the parent HC≡P polymerizes above −124 °C. In the case of the phenylogues **2a**−**d**, their relative reactivities may be less affected by the steric hindrance around the triple bond, because the degree of hindrance is similar among these compounds, so we can observe the almost purely electronic effect of the para substituents.

The dimethylamino-substituted arylphosphaethyne **2c** decomposed within a week at room temperature in air. On the other hand, **2d**, as well as **2a**, was extremely stable and no significant decomposition was observed even after 1 month under similar conditions. This high reactivity of **2c** may also indicate the perturbation caused by the *p*-amino group (Scheme 2), which increases the nucleophilic activity of the phosphorus atom. In fact, **2c** decomposed in the presence of methyl triflate in C_6D_6 at room temperature, while **2d** was stable in the presence of methyl triflate and no significant change was observed after several days.

As for the UV spectra of **2a**−**d** (Table 1, see also Figure 1 in the Supporting Information), a bathochromic shift of the $\pi-\pi^*$ transition and an increase of ϵ were observed with the increase of electron-donating ability, similar to the cases of para-substituted phenylacetylene derivatives and benzonitrile derivatives: this fact also is consistent with the electron delocalization caused by the electron-donating group as shown in Scheme 2.

Although attempted X-ray crystallographic analyses of **2a**,**b** failed due to the poor quality of single crystals for the analysis, the structure of **2c** was determined by X-ray crystallography (the reflections were collected at −70 °C).[20] Figure 1 shows an ORTEP[21] drawing of the molecular structure of **2c**. The P(1)−C(1)−C(2) portion

(17) Goede, S. J.; Bickelhaupt, F. *Chem. Ber.* **1991**, *124*, 2677.
(18) (a) Sugiyama, H.; Ito, S.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3802. (b) Appel, R.; Immenkeppel, M. *Z. Anorg. Allg. Chem.* **1987**, *553*, 7. (c) Yoshifuji, M.; Niitsu, T.; Inamoto, N. *Chem. Lett.* **1988**, 1733.
(19) For example: Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.
(20) Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-227150).
(21) Johnson, C. K. *Oak Ridge National Laboratory Report*, ORNL-TM-5138, Oak Ridge, TN, 1976.

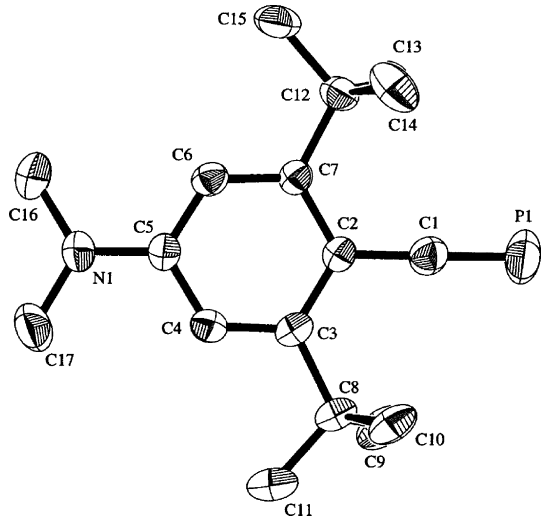


FIGURE 1. Molecular structure of **2c**, showing the atomic labeling scheme with thermal ellipsoids (50% probability). Hydrogen atoms are omitted for clarity. Some selected bond lengths (Å) and angles (deg): P(1)−C(1), 1.533(3); C(1)−C(2), 1.446(4); N(1)−C(5), 1.382(4); P(1)−C(1)−C(2), 178.7(3); C(5)−N(1)−C(16), 120.5(3); C(5)−N(1)−C(17), 120.2(3); C(16)−N(1)−C(17), 117.9(3).

is almost linear with an angle of 178.7(3)°; the value is close to that for **2d**[22] [177.0°, measured at 25 °C]. The P≡C bond length in **2c** [1.533(3) Å] is slightly longer than that for **2d** [1.516(13) Å]. The C(1)−C(2) distance of **2c** [1.446(4) Å] is longer than that for **2d** [1.427 Å]. These facts indicate that the structure of the P(1)−C(1)−C(2) moiety for **2c** slightly differs from that for **2d** in the crystal. However, the degree of the substituent effect on geometrical change seems to be small, compared with that on UV absorption.

Conclusions

In summary, we have prepared sterically protected arylphosphaethynes **2b**,**c**, bearing electron-donating groups at the para positions, as well as the para-nonsubstituted **2a**. Comparison of the spectroscopic data was carried out keeping the two *tert*-butyl groups at the ortho positions. The ^{31}P NMR chemical shifts, spin−spin coupling constants $^{1}J_{PC}$, and the UV spectra of **2b**,**c** suggest the contribution of resonance shown in Scheme 2. However, the contribution of the betaine form does not seem to be large enough, at least in the crystals, to shorten the bond distance between the sp-hybridized carbon atom and the ipso-carbon atom of the Mes* group. Further studies on structure−properties relationships and reactivities of the phosphaethynes, as well as those of phosphaethenes and diphosphenes, are in progress.

Experimental Section

2,5-Dibromo-1,3-bis(bromomethyl)benzene (4). To a solution of **3** (12.6 g, 47.7 mmol) in CCl_4 (50 mL) were added NBS (17.0 g, 95.5 mmol) and AIBN (0.4 g, 2.4 mmol). The resulting mixture was refluxed for 2 h and cooled to room temperature. Insoluble succinimide was filtered off and the solution was concentrated. Recrystallization of the residue from hexane gave 11.0 g (55% yield) of **4**: Colorless crystals, mp 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (2H, s, arom.) and 4.59 (4H, s, CH_2Br); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.6, 134.4, 125.7, 121.8, and 33.1 (CH_2Br); IR (KBr) 3129, 3069, 1533, 1431, 1263, 1209, 1111, 1024, 980, 872, and 731 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 426 ($M^+ + 8$; 4), 424 ($M^+ + 6$; 16), 422 ($M^+ + 4$; 25), 420 ($M^+ + 2$; 17), 418 (M^+; 4), 345 ($M^+ - Br + 6$; 33), 343 ($M^+ - Br + 4$; 98), 341 ($M^+ - Br + 2$; 100), 339 ($M^+ - Br$; 35), 264 ($M^+ - 2Br + 4$; 18), 262 ($M^+ - 2Br + 2$; 32), 260 ($M^+ - 2Br$; 17), 183 ($M^+ - 3Br + 2$; 13), 181 ($M^+ - 3Br$; 14), and 102 ($M^+ - 4Br$; 49). Found: *m*/*z* 421.7165. Calcd for $C_8H_6{}^{79}Br_2{}^{81}Br_2$: M, 421.7165.

2,5-Dibromo-1,3-bis(cyanomethyl)benzene (5). To a solution of **4** (42 g, 0.10 mol) in acetonitrile (500 mL) were added 18-crown-6 (5.3 g, 0.02 mol), KCN (14.0 g, 0.22 mol), water (40 mL), and a small amount of KI at room temperature. After being stirred for 24 h, the reaction mixture was worked up with water and AcOEt. The organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2) of the residue provided 28.2 g (90% yield) of **5**: Colorless crystals, mp 134−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (2H, s, arom.) and 3.87 (4H, s, CH_2CN); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 133.7, 133.0, 124.1, 122.7, 116.4, and 25.8 (CH_2); IR (KBr) 3166, 3104, 2991, 2935, 2249, 1728, 1566, 1427, 1404, 1236, 1130, 1026, 923, and 849 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 316 ($M^+ + 4$; 6), 314 ($M^+ + 2$; 13), 312 (M^+; 6), 289 ($M^+ - CN + 3$; 9), 287 ($M^+ - CN + 1$; 19), 285 ($M^+ - CN - 1$; 10), 235 ($M^+ - Br + 2$; 48), 233 ($M^+ - Br$; 47), 208 ($M^+ - Br - CN + 1$; 27), 206 ($M^+ - Br - CN - 1$; 29), 154 ($M^+ - 2Br$; 60), and 127 ($M^+ - 2Br - CN - 1$; 100). Found: *m*/*z* 311.8892. Calcd for $C_{10}H_6Br_2N_2$: M, 311.8898.

2,5-Dibromo-1,3-bis(1-cyano-1-methylethyl)benzene (6). To a solution of **5** (28.2 g, 89.8 mmol) in dimethyl sulfoxide (200 mL) was added KOH (30 g) with cooling by using an ice bath. Iodomethane (34 mL, 540 mmol) was then added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 days. When the reaction mixture was diluted with Et_2O, precipitates formed. The precipitate was separated by filtration and the filtrate was washed with water and brine. The precipitate was dissolved in AcOEt and the combined organic phase was dried over $MgSO_4$ and concentrated. Column chromatography (SiO_2) of the residue provided 32.3 g (87% yield) of **6**: Colorless crystals, mp 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (2H, s, arom.) and 1.91 (12H, s, Me); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.0, 130.7, 123.7, 123.0, 122.9, 38.2, and 28.7; IR (KBr) 2981, 2924, 2231, 1737, 1562, 1461, 1394, 1248, 1184, 1117, 1016, 870, and 733 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 372 ($M^+ + 4$; 18), 370 ($M^+ + 2$; 34), 368 (M^+; 18), 357 ($M^+ - Me + 4$; 9), 355 ($M^+ - Me + 2$; 22), 353 ($M^+ - Me$; 10), 330 ($M^+ - Me - CN + 3$; 48), 328 ($M^+ - Me - CN + 1$; 100), 326 ($M^+ - Me - CN - 1$; 48), 302 ($M^+ - 3Me - CN + 5$; 38), 300 ($M^+ - 3Me - CN + 3$; 77), 298 ($M^+ - 3Me - CN + 1$; 40), 264 ($M^+ - Br - CN + 1$; 23), and 262 ($M^+ - Br - CN - 1$; 24). Found: *m*/*z* 367.9518. Calcd for $C_{14}H_{14}Br_2N_2$: M, 367.9524.

2,5-Dibromo-1,3-di-*tert*-butylbenzene (1e). Method A: Under an argon atmosphere, to a solution of **6** (32.3 g, 87.3 mmol) in dry benzene (200 mL) was added 218 mmol of DIBAH (0.93 M solution in hexane) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. The mixture was carefully quenched with water, then 10% sulfuric acid was added. The resulting mixture was stirred for 6 h, diluted with $CHCl_3$, and filtered through Celite. The filtrate was washed with water and brine, and the organic phase was dried over $MgSO_4$ and concentrated to give crude **7**. The crude **7** thus obtained was dissolved in triethylene glycol (100 mL) and hydrazine monohydrate (8.9 g, 178 mmol) was added. The resulting mixture was heated at 130 °C for 2 h. The mixture was allowed to cool to room temperature and KOH (12 g, 214 mmol) was added. Then the flask was equipped with a Dean−Stark trap and the mixture was heated to 150 °C for 3 h to remove water under slightly reduced pressure.

(22) Arif, A. M.; Barron, A. R.; Cowley, A. H.; Hall, S. W. *J. Chem. Soc., Chem. Commun.* **1988**, 171.

The reaction mixture was heated at 200 °C for 2 h. The resulting mixture was allowed to cool to room temperature, diluted with hexane, and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated. Column chromatography (SiO_2, hexane) of the residue provided 6.9 g (20% yield) of **1e**. **Method B:** To a solution of **1a** (10 g, 37.1 mmol) in trimethyl phosphate (40 mL) was added Br_2 (9.5 mL, 185 mmol) and the resulting mixture was stirred at 90 °C for 10 h. Then the mixture was quenched with aq $NaHCO_3$ and aq $Na_2S_2O_3$. The organic layer was diluted with hexane and washed with water and brine. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. Column chromatography (SiO_2, hexane) of the residue provided **1e** (8.1 g, 63% yield). **1e**: Colorless crystals, mp 54−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (2H, s, arom.) and 1.59 (18H, s, *t*-Bu); ^{13}C-{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.0, 129.8, 124.1, 121.8, 38.7, and 31.1 (d, $^1J_{PC}$ = 40.1 Hz, P═C); IR (KBr) 2964, 2920, 2877, 1554, 1477, 1373, 1244, 1198, 1007, 868, and 841 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 350 (M^+ + 4; 13), 348 (M^+ + 2; 26), 346 (M^+; 14), 335 (M^+ − Me + 4; 15), 333 (M^+ − Me + 2; 31), 331 (M^+ − Me; 16), 307 (M^+ − 3Me + 6; 9), 305 (M^+ − 3Me + 4; 19), 303 (M^+ − 3Me + 2; 10), and 57 (*t*-Bu$^+$; 100). Found: *m*/*z* 345.9926. Calcd for $C_{14}H_{20}Br_2$: M, 345.9932.

(4-Bromo-3,5-di-*tert*-butylphenyl)(diphenylmethylene)-amine (1f). To a 50-mL two-neck flask were added **1e** (2.0 g, 5.75 mmol), $Pd(OAc)_2$ (27 mg, 0.11 mmol), DPPF (103 mg, 0.19 mmol), and NaO*t*-Bu (670 mg, 6.98 mmol) under argon, using Schlenk technique. The mixture was suspended in toluene (23 mL) and 1 mL (5.96 mmol) of benzophenone imine was added. The reaction mixture was vigorously stirred at 95 °C for 10 h and was allowed to cool to room temperature. The mixture was diluted with AcOEt and washed with water and brine. The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography (SiO_2, hexane−AcOEt 100:1) of the residue provided 2.5 g (97% yield) of **1f**: Yellow powder, mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.10 (10H, m, arom.), 6.80 (2H, s, arom.), and 1.44 (18H, s, *t*-Bu); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.9 (C═N), 149.8, 149.3, 140.1, 138.1, 137.0, 132.9, 131.3, 130.5, 129.8, 129.7, 129.0, 128.7, 128.7, 128.5, 120.8, 119.5, 38.5, and 31.2; IR (KBr) 2952, 2918, 2877, 1614, 1577, 1446, 1389, 1313, 1273, 1205, 1008, 973, 877, 773, and 696 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 449 (M^+ + 2; 47), 447 (M^+; 45), 352 (M^+ − Br − Me − 1; 21), 312 (M^+ − Br − *t*-Bu + 1; 59), and 165 (Ph_2C^+ − 1; 100). Found: *m*/*z* 447.1564. Calcd for $C_{27}H_{30}BrN$: M, 447.1562.

5-Amino-2-bromo-1,3-di-*tert*-butylbenzene (1g). To a solution of **1f** (2.5 g, 5.58 mmol) in THF (10 mL) was added 1 M hydrochloric acid (13 mL). The mixture was refluxed for 1 h, then made alkaline with 2 M aq NaOH, diluted with $CHCl_3$ and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Column chromatography (SiO_2, hexane−AcOEt 10:1 to 4:1) of the residue provided 900 mg (57% yield) of **1g**.

2-Bromo-1,3-di-*tert*-butyl-5-(dimethylamino)benzene (1c). To a stirred mixture of concentrated sulfuric acid (1 mL), 35% formalin (5 mL), and THF (5 mL) were added slowly a slurry of **1g** (900 mg, 3.2 mmol) and $NaBH_4$ (2.6 g, 68.7 mmol) in THF (30 mL) at 0 °C. The cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature and stirred for an additional 1 h. The reaction was then quenched by addition of water and the resulting mixture was extracted with $CHCl_3$. The organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was passed through a silica gel column (hexane−AcOEt 4:1) to give 830 mg (84% yield) of **1c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (2H, s, arom.), 3.00 (6H, s, NMe_2), and 1.64 (18H, s, *t*-Bu); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.0, 148.9, 112.2, 111.9, 41.2, 38.7, and 31.3; IR (KBr) 3008, 2977, 2946, 1595, 1483, 1414, 1396, 1342, 1269, 1203, 1064, 997, 838, and 725 cm^{-1}. Found: *m*/*z* 311.1243. Calcd for $C_{16}H_{26}BrN$: M, 311.1249.

Typical Procedure for the Preparation of 9. Under an argon atmosphere, to a solution of **1** (15.4 mmol) in THF (50 mL) was added 17.6 mmol of butyllithium (1.6 M solution in hexane) at −78 °C. After 5 min of stirring, PCl_3 (45.8 mmol) was added at −78 °C. The solution was then allowed to warm to 60 °C and stirred for 90 min. The volatiles were removed under vacuum, and then THF (30 mL) and bromoform (17.2 mmol) were added. The resulting mixture was allowed to cool to −98 °C and a THF (20 mL) solution of LDA (35.4 mmol) was added. The reaction mixture was then stirred for 15 min at −98 °C and allowed to warm to room temperature. The reaction mixture was diluted with hexane and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated. Column chromatography or recrystallization of the residue gave **9a**,**b**. Compound **9c** was used in the next reaction without further purification, because of the instability. **9a**: Colorless powder, mp 107−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (2H, d, ^3J = 8.4 Hz, arom.), 7.34 (1H, t, ^3J = 8.4 Hz, arom.), and 1.53 (18H, s, *t*-Bu); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.0 (d, J_{PC} = 2.3 Hz), 142.9 (d, J_{PC} = 57.6 Hz), 129.7, 127.1 (d, J_{PC} = 84.1 Hz), 125.8, 38.1, and 33.0 (d, J_{PC} = 6.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 269.2; IR (KBr) 2946, 2915, 2866, 1571, 1468, 1389, 1362, 1242, 1192, 1142, 1041, 798, 748, and 721 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 392 (M^+ + 2; 1), 379 (M^+ − Me + 4; 3), 377 (M^+ − Me + 2; 6), 375 (M^+ − Me; 3), 313 (M^+ − Br + 2; 41), 311 (M^+ − Br; 42), 283 (M^+ − Br − 2Me + 2; 28), 281 (M^+ − Br − 2Me; 29), 231 (M^+ − Br_2C − 1; 100), 217 (M^+ − Br_2C − Me; 83), and 175 (M^+ − Br_2C − *t*-Bu; 47). Found: *m*/*z* 391.9720. Calcd for $C_{15}H_{21}{}^{79}Br^{81}BrP$: M, 391.9728. **9b**: Colorless powder, mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (2H, s, arom.), 3.87 (3H, s, OMe), and 1.52 (18H, s, *t*-Bu); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 156.0 (d, J_{PC} = 2.8 Hz), 134.3 (d, J_{PC} = 56.7 Hz), 128.4 (d, J_{PC} = 86.3 Hz), 111.8, 55.3 (OMe), 38.3, and 33.0 (d, J_{PC} = 6.8 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 270.8; IR (KBr) 2958, 2868, 1591, 1556, 1462, 1392, 1361, 1287, 1221, 1198, 1061, 931, 864, 840, and 719 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 424 (M^+ + 4; 7), 422 (M^+ + 2; 15), 420 (M^+; 8), 343 (M^+ − Br + 2; 6), 341 (M^+ − Br; 6), 249 (M^+ − Br_2C − 1; 30), and 193 (M^+ − Br_2C − *t*-Bu; 100). Found: *m*/*z* 419.9864. Calcd for $C_{16}H_{23}Br_2OP$: M, 419.9853.

Typical Procedure for the Preparation of 2. Under argon atmosphere, a mixture of **9** (1 mmol), $NiBr_2(PPh_3)_2$ (0.1 mmol), PPh_3 (0.2 mmol), Zn (1 mmol), and tetrabutylammonium iodide (1 mmol) in THF (5 mL) was stirred for 24 h under reflux. After cooling, the reaction mixture was diluted with hexane and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated. Column chromatography (SiO_2, hexane) of the residue afforded the desired phosphaethyne **2**. **2a**: Colorless powder, mp 70−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (2H, d, ^3J = 8.0 Hz, arom.), 7.23 (1H, t, ^3J = 8.0 Hz, arom.), and 1.71 (18H, s, *t*-Bu); ^{13}C-{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.3 (d, $^1J_{PC}$ = 54.0 Hz, CP), 157.5 (d, J_{PC} = 6.3 Hz), 129.2 (d, J_{PC} = 5.7 Hz), 127.9 (d, J_{PC} = 21.8 Hz), 124.4 (d, J_{PC} = 1.6 Hz), 37.1, and 31.1 (d, J_{PC} = 1.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.2; UV (CH_2Cl_2) 315 (log ϵ 4.03) and 330 nm (3.94); IR (KBr) 3052, 3008, 2861, 2723, 1520, 1461, 1387, 1360, 1250, 1203, 802, and 748 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 232 (M^+; 11), 217 (M^+ − Me; 21), 199 (M^+ − P − 2; 31), 175 (M^+ − *t*-Bu; 98), 161 (M^+ − *t*-Bu − Me + 1; 98), and 143 (M^+ − *t*-Bu − P − 1; 100). Found: *m*/*z* 232.1376. Calcd for $C_{15}H_{21}P$: M, 232.1381. **2b**: Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (2H, s, arom.), 3.86 (3H, s, OMe), and 1.69 (18H, s, *t*-Bu); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.9 (d, $^1J_{PC}$ = 52.4 Hz, CP), 160.1 (d, J_{PC} = 5.6 Hz), 159.4 (d, J_{PC} = 5.6 Hz), 120.9 (d, J_{PC} = 21.8 Hz), 110.2, 55.4 (OMe), 37.4, and 31.0 (d, J_{PC} = 1.5 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 32.4; UV (CH_2Cl_2) 330 nm (log ϵ 4.22); IR (neat) 2978, 2925, 2771, 1595, 1533, 1460, 1396, 1290, 1222, 1070, 873, 848, and 764 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 262 (M^+; 100), 247 (M^+ − Me; 29), 205 (M^+ − *t*-Bu; 40), and 191 (M^+ − *t*-Bu − Me + 1; 27). Found: *m*/*z* 262.1481. Calcd

for $C_{16}H_{23}OP$: M, 262.1487. **2c**: Yellow prisms, mp 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (2H, s, arom.), 3.07 (6H, s, NMe), and 1.71 (18H, s, *t*-Bu); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4 (d, $^1J_{PC}$ = 49.8 Hz, CP), 159.4 (d, J_{PC} = 5.6 Hz), 149.6 (d, J_{PC} = 4.7 Hz), 116.1 (d, J_{PC} = 21.7 Hz), 107.9, 40.4 (NMe), 37.6, and 31.1 (d, J_{PC} = 1.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 32.1; UV (CH_2Cl_2) 377 nm (log ϵ 4.50); IR (KBr) 3037, 2954, 2715, 1599, 1525, 1487, 1421, 1338, 1261, 1203, 1057, 989, 841, and 756 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 275 (M^+; 43), 218 ($M^+ - t$-Bu; 35), 190 ($M^+ - t$-Bu − 2Me + 2; 99), and 162 ($M^+ - 2t$-Bu + 1; 100). Found: *m*/*z* 275.1797. Calcd for $C_{17}H_{26}NP$: M, 275.1803. **2d**: UV (CH_2Cl_2) 320 (log ϵ 4.17) and 334 nm (4.09).

Acknowledgment. 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.

Supporting Information Available: Experimental procedures for the preparation of 4-bromo-3,5-xylidine and **3**, UV−vis spectra of **2a**−**d** (Figure 1), UV−vis spectra of *p*-MeO-$C_6H_4C{\equiv}CH$, *p*-$(Me_2N)C_6H_4C{\equiv}CH$, *p*-$MeOC_6H_4CN$, and *p*-(Me_2N)-C_6H_4CN (Figure 2), ^{13}C NMR spectra for compounds **1e**, **1f**, **2a**−**c**, **4**−**6**, **9a**,**b**, and X-ray data in CIF format for **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049571Q