

The Electronic Effects of Bulky Aryl Substituents on Low Coordinated Phosphorus Atoms in Diphosphenes and Phosphaalkenes by Functionalization at the Para Position

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The electronic effects of bulky aryl substituents on low coordinated phosphorus atom(s) in diphosphenes and phosphaalkenes have been examined by means of functionalization at the para position of the substituents. Bulky bromobenzenes bearing an electron-donating or electron-withdrawing group at the para position were prepared as precursors of the substituents and some of them were applied to preparations of the corresponding diphosphenes and fluorenylidene(phenyl)phosphines bearing low-coordinated phosphorus atom(s). Electronic perturbation by the para-substituent in the system was indicated by UV–vis spectra and ^{31}P NMR chemical shifts. These observations can be attributed to effects induced by electronic properties of the bulky aryl substituent(s) on the lone pair of the low-coordinated phosphorus atom.

Kinetic stabilization with bulky aryl substituents such as 2,4,6-tri-*t*-butylphenyl (abbreviated to Mes*),[1] 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl,[2] and *meta*-terphenyl ligand[3] plays an important role in modern heavier main group element chemistry.[4] Kinetic stabilization has been successfully applied to studies on multiple bonds between the heavier main group elements: This stabilization method has been supposed not to perturb the electronic character and is superior to thermodynamic stabilization, at least for the purpose of studying the genuine electronic character of such bonds.[1,5]

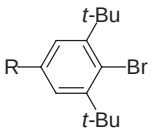
However, thermodynamic stabilization (or destabilization) and tuning of reactivity and electronic character are still attractive from the viewpoint of applications in material science. For example, if the electronic effect of the substituent is well understood, it may be possible to control the reactivity of the multiple bonds. In addition, knowledge about the structure–property relationships may become a useful guide for the design of new materials.

Although some diphosphenes[1] bearing an electron-donating or an electron-withdrawing bulky substituent were reported,[6] there has been no systematic study. On the other hand, we and others have studied modifications of the bulky aryl substituents at the ortho position(s)[7] and we applied the modified bulky substituents to the studies of multiply bonded phosphorus compounds, focusing on intramolecular interactions. We thus prepared various compounds, such as dithioxophosphoranes,[7a,e,h] diselenoxophosphoranes,[7a,e,h] and phosphaalkenes.[7i] However, such modifications often led to decreases in the degree of steric hindrance or insufficient stabilization for systematic studies on electronic properties. In the present paper, we report on modifications of the bulky Mes* group as well as preparation of diphosphenes and phosphaalkenes bearing the modified substituents: an electron-donating group or electron-withdrawing group was introduced into the para position while retaining both *ortho*-*t*-butyl groups.[8]

Such modifications do not decrease the degree of steric hindrance around the reactive center, and the kinetic stabilizing ability is expected to be conserved. In other words, the molecular design of para-modification overcomes the problems with ortho-modification. Furthermore, the electronic effect of the para-substituent may be analyzed by Hammett values.[9] It is expected that the modified bulky aryl substituents will work as useful tools for exploring reaction mechanisms by using linear free energy relationships.[10]

Results and Discussion

Preparations of Bulky Bromobenzenes Bearing a Functional Group at the Para Position. At first, we prepared bulky bromobenzene derivatives **1a–g** (Chart 1) as possible precursors of low coordinated phosphorus compounds. Although the synthesis of **1a** starting from 2,6-di-*t*-butyl-4-nitroaniline was reported by Rundel in 1968,[11] the route contained some elaborate separation processes.[12] Compound **1b** was prepared by direct bromination of 1,3,5-tri-*t*-butylbenzene with bromine in trimethyl phosphate.[13] As for the other bromobenzenes, however, similar bromination of other 1-functionalized 3,5-di-*t*-butylbenzenes such as 3,5-di-*t*-butylanisole or 3,5-di-*t*-butylaniline gave undesired 2-bromo derivatives. Thus, we developed an alternative synthetic method for **1a** and **1c**, starting from **2a**[14] and **2c**[15] via compounds **3–5** (Scheme 1): Cyanation of **2a**,**c** gave **3a**,**c**, which were methylated to give **4a**,**c**.



1a: R = H; **b**: R = *t*-Bu; **c**: R = OMe;
d: R = NMe_2; **e**: R = CO_2Me; **f**: R = CN;
g: R = I; **h**: R = Br; **i**: R = Li; **j**: R = CO_2H;
k: R = $CONH_2$; **l**: R = CF_3

Chart 1.

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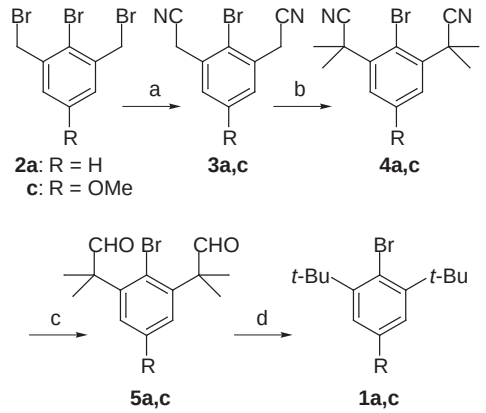


Scheme 1. Preparations of bulky bromobenzenes. a) KCN, 18-crown-6, KI, MeCN; b) MeI, KOH, DMSO; c) DIBAH, C_6H_6, then 10% H_2SO_4; d) $H_2NNH_2 \cdot H_2O$, KOH, triethylene glycol.

Reduction of **4a**,**c** with DIBAH (diisobutylaluminium hydride) formed **5a**,**c**, which were then subjected to Wolff–Kishner reduction (the Huang–Minlon method) to afford **1a**,**c**.

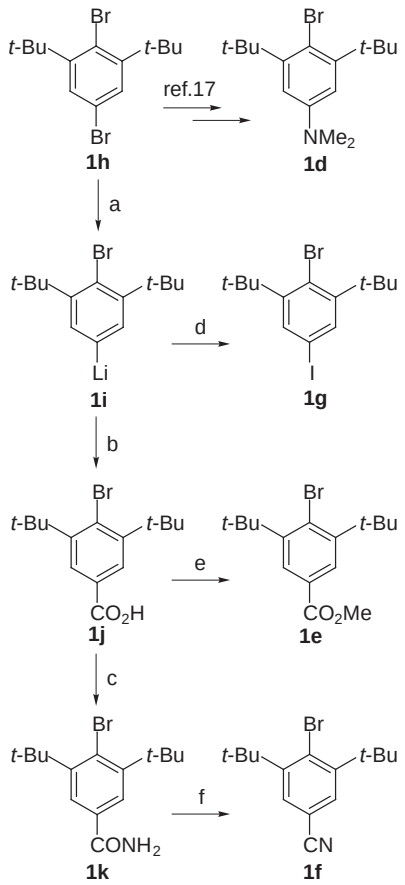
A similar synthetic route to **1d** was then investigated, starting from 2-bromo-5-(dimethylamino)-1,3-dimethylbenzene (**6**).[16] However, an attempted bromination of **6** with NBS failed to form 2-bromo-1,3-bis(bromomethyl)-5-(dimethylamino)benzene. We thus prepared **1d** from **1h** (Scheme 2) as previously reported.[17]

Novel bromobenzenes **1e**,**f** bearing electron-withdrawing groups, as well as bromoiodobenzene **1g**, were also prepared from **1h**[17] (Scheme 2). Regioselective lithiation of **1h** with butyllithium, followed by treatment with an excess amount of dry ice, afforded carboxylic acid **1j** in 70% yield. The compound **1j** was then converted to the methyl ester **1e** by reaction with iodomethane in the presence of K_2CO_3. Moreover, **1j** was converted into amide **1k**, which was then dehydrated with thionyl chloride to give nitrile **1f**.

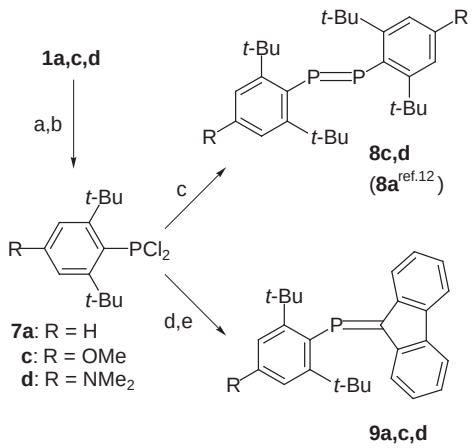
Attempted preparation of 2-bromo-1,3-di-*t*-butyl-5-(trifluoromethyl)benzene (**1l**) by using trialkyl(trifluoromethyl)silane was unsuccessful. Compound **1g** was subjected to Fuchikami's conditions;[18] however, the desired compound was not obtained in good yield.

Preparations of Diphosphenes and Fluorenylidene(phenyl)phosphines. As some para-functionalized bulky bromobenzenes were obtained, we applied these substituents to diphosphenes as steric protecting groups (Scheme 3). Lithiation of bromobenzenes **1a**,**c**,**d** with butyllithium followed by reaction with PCl_3 gave dichlorophosphines **7a**,[12] **7c**, and **7d**.[17] Dichlorophosphines **7c** [^{31}P NMR (THF–C_6D_6) δ_P 153.3] and **7d** were treated with Mg turnings in THF. *para*-Methoxy substituted diphosphene **8c** was obtained in 12% yield. Although the formation of **8d** was observed by ^{31}P NMR spectroscopy [δ_P ($CDCl_3$) 500.6], it turned out to be air and moisture sensitive and an attempted isolation of **8d** was unsuccessful. Unfortunately, attempted conversion of bromobenzenes **1e**,**f**, bearing electron-withdrawing groups to the corresponding diphosphenes **8e**,**f** failed, due to unsuccessful preparations of dichlorophosphines **7e**,**f**, respectively.[19]

Our interest was then focused on the preparation and elucidation of the properties of fluorenylidene(phenyl)phosphines. Reactions of **7c**,**d** with 9-trimethylsilyl-9-fluorenyllithium, followed by treatment with tetrabutylammonium fluoride (TBAF), gave phosphaalkenes **9c**,**d**. Compound **9a** was also obtained by a similar method, whereas **9b** was prepared according to a method reported in the literature.[20] Because at-

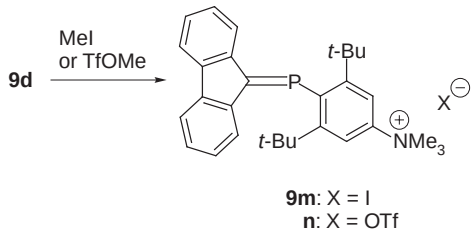


Scheme 2. Preparations of bulky bromobenzenes. a) *n*-BuLi, THF; b) CO_2(s), then aq HCl; c) $SOCl_2$, $CHCl_3$, aq NH_3; d) I_2; e) MeI, K_2CO_3, DMF; f) $SOCl_2$.



Scheme 3. Syntheses of **8c**,**d** and **9a**,**c**,**d**. a) *n*-BuLi, THF; b) PCl_3; c) Mg, THF; d) 9-trimethylsilyl-9-fluorenyllithium, THF; e) TBAF, THF.

tempted preparations of **7e**,**f** were unsuccessful, as mentioned above, we sought an alternative approach (i.e., quaternalization of the amino group) for the introduction of an electron-withdrawing group into fluorenylidene(phenyl)phosphines. As shown in Scheme 4, **9d** was allowed to react with MeI or MeOTf in C_6D_6 to form the corresponding ammonium salts **9m** or **9n**, respectively. In the ^{1}H NMR spectra of **9m** (**9n**),



Scheme 4. Preparation of **9m**,**n**.

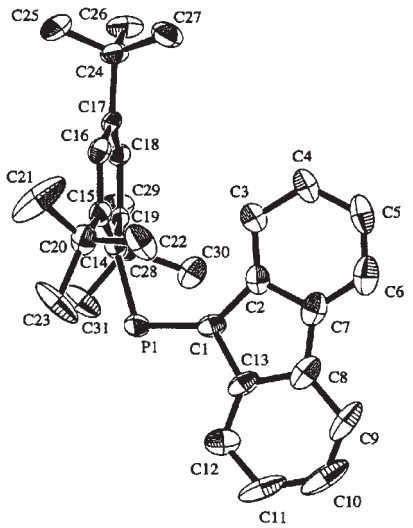


Fig. 1. Molecular structure of **9b** showing the atomic labeling scheme with thermal ellipsoids (50% probability).

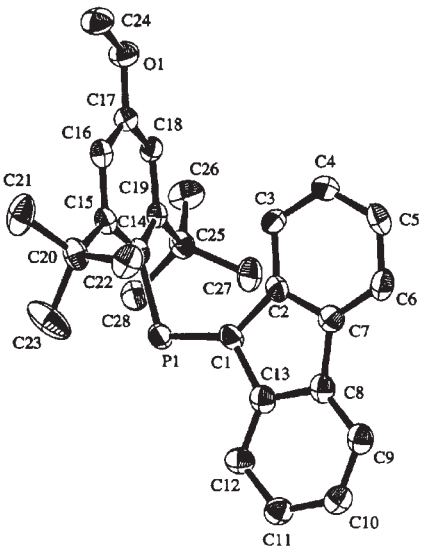


Fig. 2. Molecular structure of **9c** showing the atomic labeling scheme with thermal ellipsoids (50% probability).

singlet signals at $\delta = 4.22$ (3.90) are assignable to the N^+Me_3 protons. It should be mentioned that methylation on phosphorus will lead to a doublet in the ^{1}H NMR spectrum. The ^{31}P NMR signal for **9m**,**n** appeared in the normal phosphaalkene region; this fact also indicates that the methylation occurred on the nitrogen atom.

Structures of Diphosphenes and Fluorenylidene(phenyl)phosphines. Results of X-ray crystal analysis of the diphosphene **8c** have been reported in a previous communication.[8a] Structures of the fluorenylidene(phenyl)phosphines **9b–d** were unambiguously determined by X-ray crystallography (Figs. 1–3). Attempted analyses of compounds **9a**,**m**,**n** have been unsuccessful because of lack of crystals suitable for X-ray analyses.

Tables 1 and 2 list some important bond lengths and angles for **8b**,**c** and **9b–d**, respectively. The P=P bond length for **8c** is slightly longer than that for **8b**. The P–C_{ipso} bonds between the two diphosphenes are close in value (1.860–1.869 Å). The P–P–C bond angles in **8c** (av. 99.6°) are smaller than those in **8b**

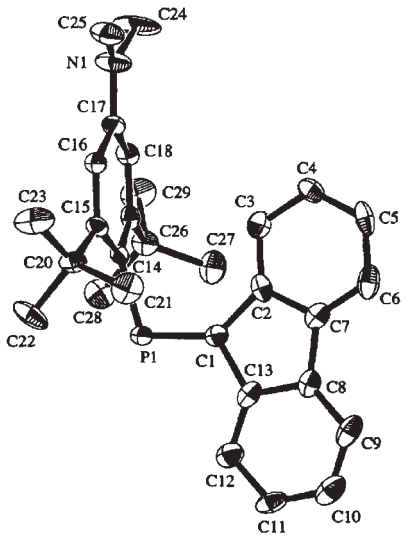
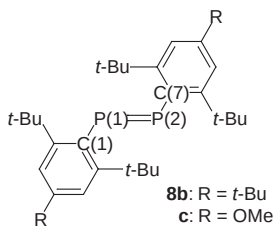


Fig. 3. Molecular structure of **9d** showing the atomic labeling scheme with thermal ellipsoids (50% probability).

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for Diphosphenes



Length or Angle	**8b**[a)]	**8c**[b)]
P(1)=P(2)	2.034(2)	2.043(1)
P(1)–C(1)	1.862(2)	1.860(4)
P(2)–C(7)	1.862(2)	1.869(4)
P(1)–P(2)–C(7)	102.8(1)	98.7(1)
P(2)–P(1)–C(1)	102.8(1)	100.5(1)
C(1)–P(1)–P(2)–C(7)	172.2(1)	165.0(2)

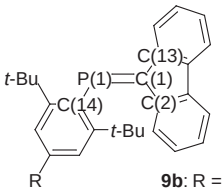
a) Data taken from Ref. 1a. b) Data taken from Ref. 8a.

(102.8°). Although the deviation from planarity is relatively large for the P=P π system in **8c** [torsion angle for C–P=P–C: 165.0(2)°], the P=C π systems in **9b**,**c** are nearly planar and **9d** deviates from planarity only slightly [C(14)–P(1)–C(1)–C(13): 175.0(4)°]. The P=C bond lengths for **9b–d** are similar within the difference of 0.008 Å. Again the P–C_{ipso} bonds are very close in value among the three fluorenylidene(phenyl)phosphines and the C–P–C angle becomes slightly smaller as the electron-donating ability of the para substituent increases. The change in the C–P–C angles may indicate that electron-donating groups decrease the degree of hybridization of the phosphorus atom. As for the other bond lengths and angles concerning the P=C π system, relations are unclear between the geometrical values and the electron-donating abilities of the substituents.

Properties of Diphosphenes and Fluorenylidene(phenyl)phosphines. Table 3 shows ^{31}P NMR and UV–vis data for **8a–d**, **9a–d**, and **9m**,**n**. Increasing electron-donating ability of the para-substituent causes a shift to lower field in ^{31}P NMR: the order of the δ_P values is **a** (488.7) < **b** (490.0) < **c** (495.9) < **d** (500.6) for diphosphenes and **m** (238.3), **n** (238.8) < **a** (254.8) < **b** (256.5) < **c** (258.0) < **d** (264.8) for the fluorenylidene(phenyl)phosphine series. In contrast, the effect of substituent on the ^{13}C NMR chemical shift for the P=C carbon is very small among compounds **9**. Figure 4 shows the relation between the ^{31}P NMR chemical shifts and the Hammett σ values of the para-substituents. Both compounds **8** and **9** show good correlation with similar correlation factors.

In the case of UV–vis spectra (Figs. 5–7), the electron-donating substituents at the para position cause bathochromic shifts of the absorption band of longest wavelength (compared with the spectra of **8a** and **9a**), although red shifts are also observed in the case of trimethylammonium derivatives **9m**,**n**. Contrary to this, absorption bands of shorter wavelengths are less affected by the para substitution. The bands of longest wavelength of diphosphenes are generally assigned to the n → π^* transition and the bands of longest wavelength for **8a–c** are also assignable to the n → π^* transition (see below). The results indicate that the para substituents strongly affect

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for Fluorenylidene(phenyl)phosphines



9b: R = *t*-Bu
c: R = OMe
d: R = NMe_2

Length or Angle	**9b**	**9c**	**9d**
P(1)=C(1)	1.701(6)	1.693(4)	1.695(5)
P(1)–C(14)	1.832(8)	1.833(4)	1.834(6)
C(1)–C(2)	1.47(1)	1.483(6)	1.480(7)
C(1)–C(13)	1.484(10)	1.491(6)	1.475(7)
P(1)–C(1)–C(13)	118.1(6)	119.4(3)	119.9(4)
P(1)–C(1)–C(2)	135.0(6)	135.7(3)	134.9(4)
C(14)–P(1)–C(1)	105.0(4)	104.6(2)	103.9(2)
C(14)–P(1)–C(1)–C(13)	−177.9(6)	178.0(3)	175.0(4)

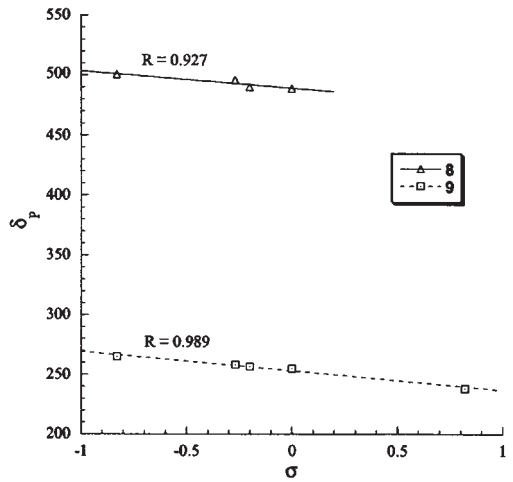


Fig. 4. Relations between ^{31}P NMR chemical shift and Hammett σ value for compounds **8** and **9**. R: correlation factor.

Table 3. Selected ^{31}P NMR (162 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), and UV–Vis Data for **8a–d**, **9a–d**, and **9m**,**n**

Compd	δ_P[a)]	δ_C ($^1J_{PC}$/Hz)[b)]	λ/nm (log ε)				
8a	488.7[c)]	—	290 (4.03)[c,d)]	340 (3.85)	450 (3.00)		
8b	490.0[e)]	—	284 (4.19)[d,f)]	340 (3.89)	460 (3.13)		
8c	495.9	—	291 (4.21)[d)]	346 (3.75)	477 (3.12)		
8d	500.6	—					
9a	254.8	170.3 (42.2)	266 (4.40)[g)]	275 (4.45)	362 (4.25)		
9b	256.5[h)]	170.3 (42.7)	256 (4.30)[g)]	275 (4.32)	365 (4.05)		
9c	258.0	171.2 (43.2)	266 (4.42)[g)]	275 (4.46)	369 (4.30)	418 (sh, 3.52)	
9d	264.8	171.3 (44.2)	267 (4.59)[g)]	275 (4.61)	361 (4.27)	374 (4.28)	443 (3.25)
9m	238.3	171.6 (42.3)	268 (4.41)[d)]	276 (4.44)	366 (4.21)	376 (4.21)	
9n	238.8[i)]	171.6 (42.3)[i)]	267 (4.43)[d)]	276 (4.47)	366 (4.24)	376 (4.25)	

a) Relative to external 85% H_3PO_4. b) Signal due to the P=*C* carbon of compound **9**. c) Data taken from Ref. 12. d) Measured in CH_2Cl_2. e) Data taken from Ref. 21. f) Data taken from Ref. 1a. g) Measured in hexane. h) Data taken from Ref. 6i, see also Ref. 20. i) Measured in CD_2Cl_2.

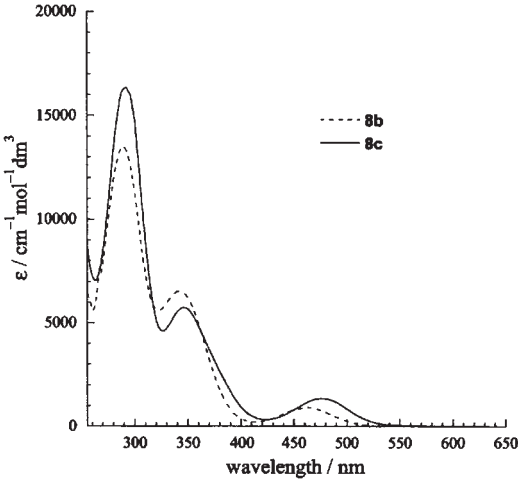


Fig. 5. UV–vis spectra for diphosphenes **8b**,**c** in CH_2Cl_2.

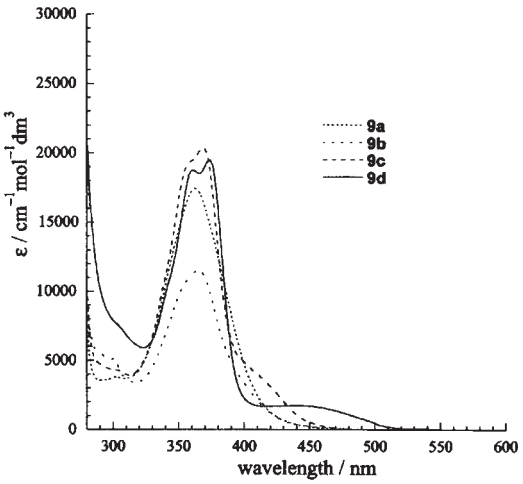


Fig. 6. UV–vis spectra for fluorenylidene(phenyl)phosphines **9a–d** in hexane.

the n $\rightarrow \pi^*$ transition of the diphosphenes **8**, whereas the effect to the $\pi \rightarrow \pi^*$ is small. As for the absorption of fluorenylidene(phenyl)phosphines, Bickelhaupt et al. reported the UV–vis spectra of (fluorenylidene)(mesityl)phosphine or (fluorenylidene)(xylyl)phosphine; however, the bands of longest wavelength have not been assigned to either n $\rightarrow \pi^*$ or $\pi \rightarrow \pi^*$.[22a]

We postulate that these absorption bands overlap each other in the case of **9**. The red shift observed in **9b–d** (compared to that of **9a**) suggests, taking the results of **8** into account, that the para substituents also affect the n $\rightarrow \pi^*$ transition of **9**, whereas the effect to the $\pi \rightarrow \pi^*$ transition is small. Due to the red shift, in the case of **9d**, the n $\rightarrow \pi^*$ transition (λ_{max} 443 nm) is well separated from the $\pi \rightarrow \pi^*$ transition. It should be mentioned that the phosphorus π bond and the aromatic π-system of the bulky aryl substituent are nearly orthogonal due to the steric hindrance of the *ortho t*-butyl groups in both compounds **8** and **9**, making the effect of the para-substituent on the $\pi \rightarrow \pi^*$ transition less effective. In other words, the electron-donating group affects mainly the electronic states of the phosphorus lone pair (n orbital) and the degree

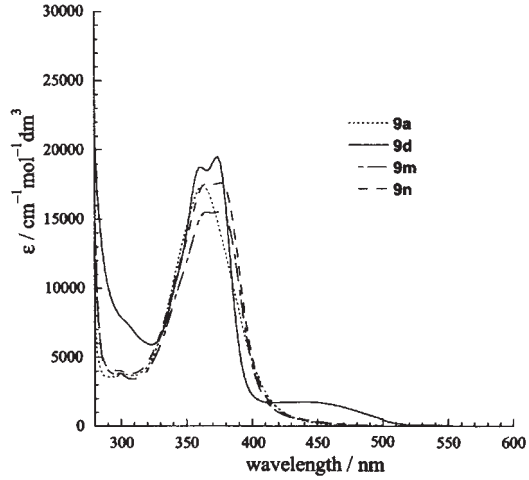


Fig. 7. UV–vis spectra for fluorenylidene(phenyl)phosphines **9a**,**d**,**m**,**n** in hexane.

of the effect depends on the contribution of the 3p atomic orbital of the phosphorus atom in the nonbonding molecular orbital.

A correlation between the chemical shift in NMR spectroscopy and the n $\rightarrow \pi^*$ absorption wavelength in UV–vis spectroscopy has been noted in some cases.[23a] In the cases of compounds **8a–d** and **9a–d**, the wavelength of the absorption band of longest wavelength correlates with the δ_P value. This fact indicates that the electron-donating groups at the para position affect both the n $\rightarrow \pi^*$ transition and the chemical shift. The observed red shift of the n $\rightarrow \pi^*$ transition may indicate that the energy level of the n orbital is increased by the electron-donating groups (see below) and that the energy gap decreases between the n orbital and the π^* orbital, because the π^* orbital containing the phosphorus atom does not seem to be affected so much due to the geometrical reason mentioned above. Any decrease in the energy gap leads to a low field shift of δ value of multinuclear NMR, because the energy gap ΔE is in inverse proportion to the deshielding paramagnetic term σ_p in the shielding constant σ.[23b,c]

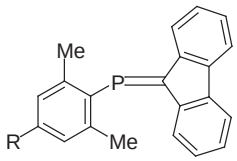
In contrast, amino group-substituted phosphaalkene Me_2N–P=C($SiMe_3$)Ph (δ_P 248) shows a shift to higher field, compared with MeO–P=C($SiMe_3$)Ph (δ_P 305) or *t*-Bu–P=C-($SiMe_3$)Ph (δ_P 290 and 328, mixture of isomers).[24] In this case, it is likely that the directly bound heteroatom (nitrogen or oxygen) affects the P=C π-system by interaction of the heteroatom lone pair with the P=C π^* orbital rather than with the n orbital.

Theoretical calculations for compounds **9a**,**9c**,**9d** [HF/6-31+G(d) level] and model compounds **10a**,**c**,**d** [where *t*-Bu was replaced by Me (Chart 2); calculated at the B3LYP/6-31G(d) level], were carried out in order to gain insight into the molecular orbitals (Table 4). Because of the geometrical requirement mentioned above, optimizations were done starting from structures in which the phosphorus π bond and the aromatic π-system of the bulky aryl substituent are nearly perpendicular. In the cases of **9a**,**c**,**d** and **10a**,**c**,**d**, the HOMO corresponds to a nonbonding orbital while the LUMO and the HOMO−1 correspond to π^* and π orbitals, respectively. The energy level of the HOMO is increased by electron-donat-

Table 4. Results of Calculation: Optimized P=C Bond Length (Å), Selected MO levels (eV), LUMO–HOMO Energy Gap (eV), and ^{31}P NMR Chemical Shift (δ_P) of **9**[a] and **10**[b]

Compd	P=C$_{calcd}$	LUMO	HOMO	HOMO−1	$\Delta_{LUMO-HOMO}$	$\delta_{P(calcd)}$[c]
9a	1.6674	0.85	−7.75	−7.90	8.60	269[d]
9c	1.6680	0.89	−7.70	−7.87	8.59	279[d]
9d	1.6683	0.98	−7.59	−7.603	8.57	263[d]
10a	1.7026	−2.34	−5.83	−5.87	3.49	270[e]
10c	1.7032	−2.28	−5.75	−5.78	3.47	272[e]
10d	1.7035	−2.17	−5.06	−5.67	2.89	269[e]
10o	1.7044	−4.72	−7.98	−8.16	3.26	199[e]
10p	1.7043	−4.68	−7.95	−8.11	3.27	198[e]

a) Calculated at the HF/6-31+G(d) level. b) Calculated at the B3LYP/6-31G(d) level. c) Relative to PMe_3 ($\delta_P - 62$), calculated by the GIAO method. d) Calculated at the HF/6-31G(d) level. e) Calculated at the B3LYP/6-31+G(d,p) level.



10a: R = H
c: R = OMe
d: R = NMe_2
o: R = $N^+(H)Me_2$
p: R = N^+Me_3

Chart 2.

ing groups (**9d** > **9c** > **9a**). The calculated order of the HOMO–LUMO gaps [**9d** < **9c** < **9a**] corresponds to the tendency of the red-shift in the UV–vis spectra. GIAO calculations of ^{31}P NMR chemical shifts for **9a**,**c**,**d** and **10a**,**c**,**d** showed δ_P to be in the 260–270 region, which is in relatively good agreement with the experimental data, however, the suggested order of the chemical shift [δ_P (**9c**) (lower field) > δ_P (**9a**) > δ_P (**9d**) (higher field)] is inconsistent with the experimental results. Probably, the differences among the three compounds are small and beyond the accuracy of the method. In the cases of **10o** and **10p** (Chart 2) as models for **9m** and **9n**, respectively, the HOMO is a π orbital while the HOMO−1 corresponds to a nonbonding orbital. The calculated HOMO–LUMO gaps for **10o**,**p** correspond to the experimentally observed slightly red-shifted absorption band of the longest wavelength in the UV–vis spectra for **9m**,**n** (compared to **9a**) and the calculated δ_P corresponds to up-field shift in the ^{31}P NMR spectra, although the effects of counter anion and solvent were not taken into account in these calculations.

Conclusion

In summary, we have developed synthetic routes to some bulky bromobenzenes bearing electron-donating substituents or electron-withdrawing substituents at the para position. Some low-coordinated phosphorus compounds bearing such substituents were prepared and the para-substituent effect was evaluated by NMR and UV–vis spectroscopies as well as by theoretical calculations. The electronic effects of the para-substituent were evaluated in terms of Hammett parameters and a structure–property relationship was demonstrated. It was revealed that electron-donating groups at the para position increase the reactivity of the low coordinated phosphorus compounds, although the phosphorus π-bond and the aryl groups are nearly orthogonal. Most of the previously reported sterically protecting groups are designed not to perturb the electronic character of the multiple bonds of the heavier main group elements; however, our present study revealed that well designed bulky aryl substituents can protect the unstable bond and change its electronic character and reactivity at the same time. This basic understanding may become a useful guide for new protecting groups and lead to the development of new materials[25] or catalysts.[26] The results reported here will lead to prediction and control of the properties and reactivity of phosphaalkenes and diphosphenes, as well as other compounds containing multiple bonds between the heavier main group elements.

Experimental

Melting points were measured on a Yanagimoto MP-J3 micro melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance-400 or a Bruker AM-600 spectrometer. UV spectra were measured on a Hitachi U-3210 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. MS spectra were taken on either a JEOL HX-110 or a Hitachi M-2500S spectrometer. FT-ICR-MS spectra were measured on a Bruker APEX III spectrometer. X-ray diffraction data were collected on a Rigaku R-AXIS IV diffractometer. Reactions were performed under an argon atmosphere, unless otherwise specified.

2-Bromo-1,3-bis(cyanomethyl)benzene (3a). To a solution of **2a** (10.5 g, 30.6 mmol) in MeCN (170 mL) were added 18-crown-6 (2.0 g, 7.63 mmol), KCN (5.76 g, 88.5 mmol), H_2O (20 mL), and KI (0.3 g, 1.8 mmol) at room temperature. After being stirred for 24 h, the reaction mixture was diluted with water and extracted with EtOAc. The organic extracts were washed with brine, and then dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (silica gel, chloroform) to afford **3a** (6.94 g, 96% yield): Colorless solid, mp 102–104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.45 (m, 3H), 3.88 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 132.0 (*o*-arom.), 130.2 (*m*-arom.), 129.0 (*p*-arom.), 125.4 (Br–C), 117.2 (CN), 26.0 (CH_2); IR (KBr) 3016, 3008, 2922, 2247, 1462, 1429, 1402, 1030, 766 cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel intensity) 236 ($M^+ + 2$; 58), 234 (M^+; 60), 209 ($M^+ - CN + 1$; 48), 207 ($M^+ - CN - 1$;

49), 155 ($M^+ - Br$; 100), and 128 ($M^+ - Br - CN - 1$; 48). Found: m/z 233.9799. Calcd for $C_{10}H_7BrN_2$: M, 233.9792. Found: C, 50.86; H, 3.13; Br, 34.04; N, 11.64%. Calcd for $C_{10}H_7BrN_2$: C, 51.09; H, 3.00; Br, 33.99; N, 11.92%.

2-Bromo-1,3-bis(1-cyano-1-methylethyl)benzene (4a). To a solution of **3a** (11.3 g, 48 mmol) in DMSO (155 mL) was added KOH (37.5 g, 0.66 mol) with cooling using an ice bath. After 15 min of stirring at 0 °C, MeI (24 mL, 0.38 mol) was added to the reaction mixture. The reaction mixture was allowed to warm to ambient temperature, and then was stirred for 40 h. When the reaction mixture was diluted with Et_2O, precipitates formed; they were collected by filtration. The filtrate was washed with water and brine, combined with a solution of the precipitates dissolved in EtOAc, and then dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (silica gel, hexane–EtOAc, 4:1) to afford **4a** (9.7 g, 69% yield): Colorless solid, mp 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.39 (m, 3H), 1.95 (s, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.1 (*o*-arom.), 128.6 (*p*-arom.), 127.6 (*m*-arom.), 124.9 (Br–C), 123.8 (CN), 38.3 ($\underline{C}Me_2CN$), 28.9 (Me); IR (KBr) 2993, 2231, 1475, 1456, 1396, 1255, 1155, 1022, 796, 727 cm^{-1}; MS (EI, 70 eV) m/z 292 ($M^+ + 2$; 79), 290 (M^+; 80), 277 ($M^+ - Me + 2$; 24), 275 ($M^+ - Me$; 24), 250 ($M^+ - Me - CN + H + 2$; 98), and 248 ($M^+ - Me - CN + H$; 100). Found: m/z 290.0421. Calcd for $C_{14}H_{15}BrN_2$: M, 290.0419. Found: C, 57.27; H, 5.20; N, 9.41%. Calcd for $C_{14}H_{15}BrN_2$: C, 57.75; H, 5.19; N, 9.62%.

2-Bromo-1,3-bis(1-formyl-1-methylethyl)benzene (5a). Under an argon atmosphere, to a solution of **4a** (9.686 g, 33.3 mmol) in dry benzene (420 mL) was added a solution of 83.7 mmol of DIBAH (0.93 M solution in hexane) at 0 °C. The reaction mixture was then allowed to warm to ambient temperature and was stirred for 2 h. The reaction mixture was quenched carefully with water; then 10% sulfuric acid was added to it and the resulting mixture was stirred for 2 h. The mixture was worked up using benzene and brine. The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (silica gel, $CHCl_3$) to provide **5a** (9.088 g, 92% yield): Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 2H, CHO), 7.49–7.42 (m, 3H), 1.55 (s, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 203.3 (CHO), 144.9 (*o*-arom.), 128.7 (*p*-arom.), 128.7 (*m*-arom.), 125.4 (Br–C), 53.2 ($\underline{C}Me_2CHO$), 24.3 (Me); IR (KBr) 2981, 2976, 2945, 2931, 1707, 1456, 1390, 1367, 1255, 1201, 1159, 1101, 1011, 845, 798, 725 cm^{-1}. Weak molecular ion peak in EI-MS.

2-Bromo-1,3-di-*t*-butylbenzene (1a). A mixture of **5a** (482.2 mg, 1.623 mmol), triethylene glycol (40 mL), KOH (551 mg), water (3.8 mL), and hydrazine monohydrate (1.6 mL) was heated at 130 °C for 2 h. The flask was then equipped with a Dean–Stark trap and the reaction mixture was heated at 200 °C for 4 h. After being cooled to room temperature, the mixture was worked up using Et_2O and brine. The organic layer was dried ($MgSO_4$) and concentrated. Removal of the solvent in vacuo afforded **1a**[11,12] (307.0 mg, 70% yield).

2-Bromo-1,3-bis(cyanomethyl)-5-methoxybenzene (3c). Similarly to **3a**, **2c** (26.8 g, 71.9 mmol) was allowed to react with KCN to give **3c** (12.0 g, 63% yield): Colorless crystals, mp 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 2H, arom.), 3.88 (s, 3H, OMe), 3.86 (s, 4H, benzyl); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.8 (MeO–$\underline{C}$), 132.7 (*m*-arom.), 116.9, 115.9, 115.2, 56.2, 26.1; IR (KBr) 2944, 2840, 2252, 1585, 1457, 1428, 1324, 1261, 1191, 1163, 1064, 1020, 945, 926, 846 cm^{-1}; MS (EI, 70 eV) m/z 266 ($M^+ + 2$; 98) and 264 (M^+; 100). Found m/z 263.9905. Calcd for $C_{11}H_9BrN_2O$: 263.9898.

2-Bromo-1,3-bis(1-cyano-1-methylethyl)-5-methoxybenzene (4c). Compound **3c** (5.33 g, 20.1 mmol) was allowed to react with MeI in the presence of KOH to give **4c** (6.3 g, quant.): Colorless crystals, mp 149.5–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H, arom.), 3.87 (s, 3H, OMe), 1.95 (s, 12H, Me); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.2, 142.2, 123.7, 114.8, 113.6, 56.0, 38.6, 28.7; IR (KBr) 2991, 2944, 2844, 2231, 1710, 1589, 1462, 1403, 1296, 1251, 1211, 1186, 1051, 1020, 877, 849, 731 cm^{-1}; MS (EI, 70 eV) m/z 322 ($M^+ + 2$; 99), 320 (M^+; 100), 280 ($M^+ - Me - CN + 1$; 20), 278 ($M^+ - Me - CN - 1$; 20), 252 ($M^+ - CMe_2CN$; 18), and 250 ($M^+ - CMe_2CN - 2$; 17). Found m/z 320.0520. Calcd for $C_{15}H_{17}BrN_2O$: 320.0524.

2-Bromo-1,3-bis(1-formyl-1-methylethyl)-5-methoxybenzene (5c). Compound **4c** (6.0 g, 18.8 mmol) was allowed to react with DIBAH to give crude **5c**. The crude product was purified by flash column chromatography (silica gel, hexane–EtOAc, 3:1) to furnish **5c** (6.1 g, quant.): Colorless crystals, mp 98–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 2H, CHO), 6.99 (s, 2H, arom.), 3.88 (s, 3H, OMe), 1.54 (s, 12H, Me); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 203.0 (CHO), 159.6, 145.9, 115.7, 114.5, 55.9, 53.2, 24.3; IR (KBr) 2979, 2943, 2881, 2803, 2707, 1710, 1587, 1463, 1400, 1298, 1213, 1126, 1053, 1022, 897, 849, 727 cm^{-1}; MS (EI, 70 eV) m/z 328 ($M^+ + 2$; 6), 326 (M^+; 6), 299 ($M^+ - CHO + 1$; 3), 297 ($M^+ - CHO$; 3), and 247 ($M^+ - Br$; 100). Found m/z 326.0521. Calcd for $C_{15}H_{19}BrO_3$: 326.0518.

2-Bromo-1,3-di-*t*-butyl-5-methoxybenzene (1c). Compound **5c** (2.0 g, 6.1 mmol) was allowed to react with hydrazine monohydrate in the presence of KOH to give **1c** (873 mg, 48% yield): Colorless crystals, mp 59–60.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H, arom.), 3.85 (s, 3H, OMe), 1.63 (s, 18H, *t*-Bu); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9 (MeO–$\underline{C}$), 151.0 (*o*-arom.), 115.9 (Br–C), 112.7 (*m*-arom.), 55.5 (OMe), 38.7 ($\underline{C}Me_3$), 31.2 ($C\underline{Me}_3$); IR (KBr) 2935, 2869, 2827, 1587, 1458, 1390, 1288, 1217, 1066, 1010, 869, 847 cm^{-1}; MS (EI, 70 eV) m/z 300 ($M^+ + 2$; 99), 298 (M^+; 100), 285 ($M^+ - Me + 2$; 32), 283 ($M^+ - Me$; 33), and 57 (t-Bu^+; 52). Found m/z 298.0934. Calcd for $C_{15}H_{23}BrO$: 298.0932.

4-Bromo-3,5-di-*t*-butylbenzoic Acid (1j). Under an argon atmosphere, to a solution of **1h** (1.04 g, 3 mmol) in THF (10 mL) was added 3.2 mmol of *n*-BuLi (1.6 M solution in hexane) at −78 °C. The mixture was added dropwise to an excess amount of crushed dry ice via a cannula. The cooling bath was removed and the solution was allowed to warm to room temperature. After stirring for an additional 30 min, the reaction was quenched by the addition of 1 M hydrochloric acid and the mixture was extracted with EtOAc. The organic phase was washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by flash column chromatography (silica gel, hexane–EtOAc, 10:1 to 2:1) to give **1j** (656 mg, 70% yield): Colorless solid, mp 150–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.8 (brs, 1H), 7.56 (s, 2H), 6.87 (s, 2H), 1.48 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 179.5, 149.6, 130.0, 128.7, 124.1, 37.4, 32.4; IR (KBr) 3456, 3113, 3089, 3026, 2983, 2960, 1700, 1568, 1394, 1369, 1286, 1253, 1205, 1083, 933, 860, 796 cm^{-1}; MS (EI, 70 eV) m/z 314 ($M^+ + 2$; 8), 312 (M^+; 9), 299 ($M^+ - Me + 2$; 34), 297 ($M^+ - Me$; 35), 281 ($M^+ - OH - O + 2$; 72), 279 ($M^+ - OH - O$; 77), 253 ($M^+ - CO_2H - Me + 1$; 81), 251 ($M^+ - CO_2H - Me - 1$; 82), and 130 ($M^+ - Br - CO_2H - t$-$Bu - 1$; 100). Found m/z 312. 0713. Calcd for $C_{15}H_{21}BrO_2$: 312.0725.

Methyl 4-Bromo-3,5-di-*t*-butylbenzoate (1e). To a solution of **1j** (217 mg, 0.7 mmol) in DMF (2 mL) were added K_2CO_3

(117 mg, 0.84 mmol) and MeI (0.1 mL, 1.6 mmol). After being stirred for 1.5 h, the reaction mixture was diluted with Et_2O. The combined organic layer was washed with water and brine. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography (silica gel, hexane–EtOAc, 10:1) to furnish **1e** as a yellow viscous oil (157 mg, 69% yield). **1e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 3.85 (s, 3H), 1.38 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.6, 149.9, 130.6, 128.6, 123.8, 52.0, 37.2, 32.2; IR (KBr) 2962, 2907, 1734, 1568, 1486, 1398, 1365, 1255, 1207, 1143, 1076, 865, 850, 788, 769 cm^{-1}; MS (EI, 70 eV) m/z 328 ($M^+ + 2$; 12), 326 (M^+; 12), 313 ($M^+ - Me + 2$; 33), 311 ($M^+ - Me$; 34), 297 ($M^+ - OMe + 2$; 43), 295 ($M^+ - OMe$; 45), 281 ($M^+ - OMe - O + 2$; 98), 279 ($M^+ - OMe - O$; 100), 253 ($M^+ - CO_2Me - Me + 1$; 81), and 251 ($M^+ - CO_2Me - Me - 1$; 67). Found m/z 326.0895. Calcd for $C_{16}H_{23}BrO_2$: 326.0881.

4-Bromo-3,5-di-*t*-butylbenzamide (1k). To a solution of **1j** (70 mg, 0.22 mmol) in $CHCl_3$ (1 mL) was added $SOCl_2$ (1 mL). After 2 h of stirring at 70 °C, volatiles were removed in vacuo. To the residue was added aqueous 30% NH_3 (1 mL), and the resulting mixture was stirred at ambient temperature for 6 h. The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water and brine. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography (silica gel, hexane–EtOAc, 10:1 to 1:2) to furnish **1k** (26.2 mg, 38% yield): Colorless crystals, mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 6.24 (s, 1H), 5.74 (s, 1H), 1.49 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.2, 150.0, 133.1, 129.0, 123.6, 37.7, 32.8; IR (KBr) 2956, 2929, 1643, 1566, 1469, 1369, 1251, 1095, 1021, 1014, 931, 891, 863, 791, 758, 702, 699 cm^{-1}; MS (EI, 70 eV) m/z 313 ($M^+ + 2$; 69), 311 (M^+; 69), 296 ($M^+ - NH_2 + 1$; 63), 294 ($M^+ - NH_2 - 1$; 48), 281 ($M^+ - NH_2 - O + 2$; 100), 279 ($M^+ - NH_2 - O$; 96), 254 ($M^+ - t$-Bu; 78), and 252 ($M^+ - t$-Bu $- 2$; 78). Found m/z 311.0874. Calcd for $C_{15}H_{22}BrNO$: 311.0885.

4-Bromo-3,5-di-*t*-butylbenzonitrile (1f). A solution of **1k** (26.2 mg, 84 μmol) in $SOCl_2$ (0.8 mL) was stirred for 3 h in an oil bath (75 °C). Volatiles were removed in vacuo, and then the residue was purified by flash column chromatography (silica gel, hexane–EtOAc, 10:1) to furnish **1f** (25.3 mg, quant.): Yellow plates, mp 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 1.57 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 128.6, 128.0, 120.9, 108.7, 32.2, 30.5; IR (KBr) 2960, 2863, 2222, 1732, 1564, 1475, 1404, 1367, 1255, 1207, 1124, 1076, 1022, 931, 862, 798 cm^{-1}; MS (EI, 70 eV) m/z 295 ($M^+ + 2$; 32), 293 (M^+; 23), 280 ($M^+ - Me + 2$; 35), 278 ($M^+ - Me$; 34), 238 ($M^+ - t$-Bu $+ 2$; 19), 236 ($M^+ - t$-Bu; 18), and 182 ($M^+ - Br - 2Me - 2$; 100). Found m/z 293.0780. Calcd for $C_{15}H_{20}BrN$: 293.0779.

2-Bromo-1,3-di-*t*-butyl-5-iodobenzene (1g). Under an argon atmosphere, to a solution of **1h** (1.04 g, 3.0 mmol) in THF (6 mL) was added 3.0 mmol of *n*-BuLi (1.6 M solution in hexane) at −78 °C. The mixture was added dropwise to a solution of I_2 (2.0 g, 7.9 mmol) in THF (2 mL). The cooling bath was removed and the solution was warmed to room temperature. After being stirred for an additional 30 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and $Na_2S_2O_3$. The reaction mixture was diluted with hexane, and washed with water and brine. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane) to give 854 mg (73% yield) of **1g**: Colorless solid, mp 42–44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H), 1.68 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.8, 129.6, 123.2, 97.8, 39.8, 32.0; IR (KBr) 2962, 2871, 1556, 1479, 1396, 1371, 1240, 1197, 1116, 987, 865 cm^{-1}; MS (EI, 70 eV) m/z 396 ($M^+ + 2$; 45), 394 (M^+; 45), 254 ($M^+ - I - Me + 2$; 23), 252 ($M^+ - I - Me$; 23), 227 ($M^+ - I - 3Me + 5$; 49), 225 ($M^+ - I - 3Me + 3$; 49), and 131 ($M^+ - I - Br - t$-Bu; 100). Found m/z 393.9822. Calcd for $C_{14}H_{20}BrI$: 393.9791.

1,2-Bis(2,6-di-*t*-butyl-4-methoxyphenyl)diphosphene (8c). Under an argon atmosphere, to a solution of **1c** (866 mg, 2.91 mmol) in THF (8 mL) was added 2.99 mmol of *n*-BuLi (1.6 M solution in hexane) at −78 °C. After 1 min of stirring at −78 °C, PCl_3 (0.76 mL, 8.5 mmol) was added to the reaction mixture. The cooling bath was removed and the solution was allowed to warm to 60 °C. After 90 min of stirring at that temperature, volatiles were removed under vacuum. The resulting crude dichlorophosphine **7c** was used in the following reaction without further purification. The residue was dissolved in THF (8 mL), and Mg turnings (70 mg, 2.92 mmol) were added to the solution at 0 °C. The resulting mixture was stirred for 1 h at room temperature. The solution was diluted with hexane, filtered to remove inorganic salts, and then concentrated. The residue was purified by flash column chromatography (silica gel, hexane–EtOAc, 100:1) to give a mixture of compounds. The mixture was further purified by GPC (toluene) to give 90 mg of **8c** (12% yield): Orange prisms, mp 165–169 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.14 (s, 4H), 3.56 (s, 6H), 1.41 (s, 36H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ 159.3, 152.6, 115.2, 108.6, 55.4, 35.3, 31.6; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 495.9; IR (KBr) 2969, 2911, 2864, 1585, 1552, 1462, 1411, 1386, 1286, 1218, 1195, 1062, 931, 860, 842, 741 cm^{-1}; UV (hexane) λ_{max} nm ($\log \varepsilon$) 290 (4.21), 347 (3.74), 478 (3.10); MS (EI, 70 eV) m/z 500 (M^+; 16), 251 (ArylP$^+ + 1$; 84), and 249 (ArylP$^+ - 1$; 100). Found m/z 500.3000. Calcd for $C_{30}H_{46}O_2P_2$: 500.2973.

1,2-Bis[2,6-di-*t*-butyl-4-(dimethylamino)phenyl]diphosphene (8d). Compound **1d** (634 mg, 2.03 mmol) was converted to **7d**, which was allowed to react with magnesium turnings to give crude **8d**. Attempted isolation of **8d** was unsuccessful: ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 500.6.

Typical Procedure for the Preparation of 9. Under an argon atmosphere, to a solution of **1** (1 mmol) in THF (2 mL) was added 1.06 mmol of *n*-BuLi (1.6 M solution in hexane) at −78 °C. After this mixture was stirred for 1 min at the temperature, PCl_3 (0.25 mL, 2.9 mmol) was added to it. The cooling bath was then removed and the solution was slowly warmed to 60 °C. After 90 min of stirring at that temperature, volatiles were removed under vacuum. The resulting crude dichlorophosphine was used for the next reaction without further purification. A THF solution of 9-trimethylsilyl-9-fluorenyllithium was prepared at −78 °C by the addition of 1.06 mmol of *n*-BuLi (1.6 M solution in hexane) to a solution of 9-(trimethylsilyl)fluorene (238 mg, 1 mmol) in THF (2 mL). This solution was added dropwise to the solution of the dichlorophosphine at −78 °C. The reaction mixture was allowed to warm to room temperature, and then 3 mmol of TBAF (1 M solution in THF) were added. After 1.5 h of stirring, the reaction mixture was diluted with EtOAc, and then washed with water and brine. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography (silica gel, hexane–EtOAc) to give **9**.

9a (86% yield): Yellow powder, mp 162–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, 1H, $J = 7.1$, 4.4 Hz), 7.64 (d,

1H, $J = 7.0$ Hz), 7.58–7.53 (3H, m), 7.47 (dd, 1H, $J = 9.0$, 6.7 Hz), 7.37–7.29 (m, 2H), 7.17 (t, 1H, $J = 7.4$ Hz), 6.78 (dd, 1H, $J = 7.5$, 7.5 Hz), 5.29 (dd, 1H, $J = 7.7$, 2.7 Hz), 1.46 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.3 (d, $J = 42.2$ Hz, P=C), 155.2, 143.3 (d, $J = 26.8$ Hz), 139.8 (d, $J = 10.0$ Hz), 138.8 (d, $J = 10.0$ Hz), 138.5 (d, $J = 9.2$ Hz), 138.4 (d, $J = 14.5$ Hz), 129.2, 128.6 (d, $J = 6.9$ Hz), 128.5 (d, $J = 6.2$ Hz), 127.3, 127.3 (d, $J = 6.9$ Hz), 126.7 (d, $J = 7.6$ Hz), 125.9, 121.0, 120.7, 119.8, 119.4, 119.3, 38.5, 33.0; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 254.8; IR (KBr) 2952, 2896, 1570, 1438, 1357, 1240, 1199, 1143, 800, 771, 731 cm^{-1}; UV (hexane) λ_{max} nm ($\log \varepsilon$) 237 (4.55), 266 (4.40), 275 (4.45), 362 (4.25); MS (EI, 70 eV) m/z 384 (M^+; 27), 219 ($ArylP^+ + 1$; 100), 165 (Fluorenyl$^+$; 28), and 57 (t-Bu$^+$; 9). Found m/z 384.2010. Calcd for $C_{27}H_{29}P$: 384.2007.

9b[20] (42% yield): UV (hexane) λ_{max} nm ($\log \varepsilon$) 238 (4.48), 266 (4.30), 275 (4.32), 365 (4.05).

9c (38% yield): Orange crystals, mp 205–206.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, 1H, $J = 7.2$, 4.4 Hz), 7.64 (d, 1H, $J = 7.2$ Hz), 7.57 (d, 1H, $J = 7.6$ Hz), 7.37–7.28 (m, 2H), 7.18 (dd, 1H, $J = 7.6$, 7.6 Hz), 7.14 (s, 2H), 6.84 (dd, 1H, $J = 7.6$, 7.6 Hz), 5.56 (dd, 1H, $J = 8.0$, 6.8 Hz), 3.96 (s, 3H), 1.44 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2 (d, $J = 43.2$ Hz, P=C), 160.4, 156.8, 143.2 (d, $J = 26.8$ Hz), 139.7 (d, $J = 10.3$ Hz), 138.8 (d, $J = 17.1$ Hz), 138.5 (d, $J = 14.5$ Hz), 129.2 (d, $J = 56.5$ Hz), 128.5 (d, $J = 6.2$ Hz), 128.4 (d, $J = 6.9$ Hz), 127.7 (d, $J = 5.6$ Hz), 127.7, 126.8 (d, $J = 7.6$ Hz), 121.0, 120.7, 119.8, 119.4, 119.3, 112.2, 55.6, 38.6, 32.8; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 258.0; IR (KBr) 2966, 2931, 2891, 2860, 1589, 1438, 1284, 1097, 1066, 1026, 804, 771, 727 cm^{-1}; UV (hexane) λ_{max} nm ($\log \varepsilon$) 239 (4.61), 266 (4.42), 275 (4.46), 369 (4.30); MS (EI, 70 eV) m/z 414 (M^+; 18) and 249 ($ArylP^+ - 1$; 100). Found 414.2104. Calcd for $C_{28}H_{31}OP$: 414.2113.

9d (14% yield): Red crystals, mp 191–193 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, 1H, $J = 7.8$, 4.4 Hz), 7.67 (d, 1H, $J = 7.2$ Hz), 7.60 (d, 1H, $J = 7.6$ Hz), 7.37–7.31 (m, 2H), 7.20 (dd, 1H, $J = 8.0$, 8.0 Hz), 7.00 (s, 2H), 6.88 (dd, 1H, $J = 7.2$, 7.2 Hz), 5.67 (dd, 1H, $J = 8.0$, 7.2 Hz), 3.03 (s, 6H), 1.48 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.3 (d, $J = 44.2$ Hz, P=C), 155.8, 151.2, 143.5 (d, $J = 26.2$ Hz), 139.5 (d, $J = 10.2$ Hz), 138.9 (d, $J = 16.8$ Hz), 138.5 (d, $J = 14.5$ Hz), 128.3 (d, $J = 2.8$ Hz), 128.2 (d, $J = 3.3$ Hz), 127.3 (d, $J = 3.7$ Hz), 127.2, 127.1, 127.1, 123.7 (d, $J = 56.1$ Hz), 121.0, 120.7, 119.8, 119.2 (d, $J = 2.3$ Hz), 111.0, 41.1, 38.7, 32.9 (d, $J = 6.8$ Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 264.8; IR (KBr) 3097, 2964, 1593, 1481, 1437, 1338, 1252, 1182, 1047, 989, 844, 775, 735 cm^{-1}; UV (hexane) λ_{max} nm ($\log \varepsilon$) 239 (4.50), 267 (4.59), 275 (4.61), 374 (4.28); MS (EI, 70 eV) m/z 427 (M^+; 1), 262 ($ArylP^+ - 1$; 80), and 206 ($ArylP^+ - t$-Bu; 100). Found m/z 427.2426. Calcd for $C_{29}H_{34}NP$: 427.2429.

[3,5-Di-*t*-butyl-4-(9-fluorenylidenephosphino)phenyl]trimethylammonium Iodide (9m). To a solution of **9d** (3.0405 mg, 7.1 μmol) in C_6D_6 (0.5 mL) in an NMR tube, was added MeI (0.2 mL, 3.2 mmol). The mixture was warmed at 50 °C for 2 h, and the solution turned light yellow. Volatiles were removed in vacuo, and the residue was washed with hexane 3 times to give 2.1 mg of **9m** (52% yield): Yellow powder, mp 168 °C (decomp.); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, 1H, $J = 8.0$, 4.0 Hz), 7.85 (s, 2H), 7.62–7.55 (m, 2H), 7.38–7.28 (m, 2H), 7.19 (dd, 1H, $J = 7.6$, 7.6 Hz), 6.77 (dd, 1H, $J = 7.6$, 7.6 Hz), 5.14 (d, 1H, $J = 8.0$ Hz), 4.22 (s, 9H), 1.51 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.6 (d, $J = 42.3$ Hz, P=C), 158.9, 148.3, 143.7 (d, $J = 62.7$ Hz), 142.7 (d, $J = 27.8$ Hz), 140.3 (d, $J = 10.9$ Hz), 138.6 (d, $J = 14.6$ Hz), 138.2 (d, $J = 17.5$ Hz), 129.6 (d, $J = 5.8$ Hz), 129.3 (d, $J = 7.3$ Hz), 127.7 (d, $J = 2.1$ Hz), 127.4 (d, $J = 2.9$ Hz), 125.6 (d, $J = 7.3$ Hz), 120.9 (d, $J = 24.8$ Hz), 120.0, 116.3, 58.4, 39.6, 32.9 (d, $J = 6.5$ Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 238.3; IR (KBr) 2952, 1738, 1577, 1473, 1442, 1398, 1363, 1246, 1198, 1130, 1043, 943, 902, 773, 729 cm^{-1}; UV (CH_2Cl_2) λ_{max} nm ($\log \varepsilon$) 268 (4.41), 276 (4.44), 366 (4.21), 376 (4.21).

[3,5-Di-*t*-butyl-4-(9-fluorenylidenephosphino)phenyl]trimethylammonium Trifluoromethanesulfonate (9n). In an NMR tube, MeOTf (0.2 mL, 1.8 mmol) was added to a solution of **9d** (2.1533 mg, 5 μmol) in C_6D_6 (0.5 mL). The mixture was shaken for 1 min, upon which the solution turned light yellow. Volatiles were removed in vacuo and the residue was washed with hexane 3 times to give 2.0 mg of **9n** (68% yield): Yellow powder, mp 250–252 °C; ^1H NMR (400 MHz, CD_2Cl_2) δ 8.25 (dd, 1H, $J = 7.6$, 4.0 Hz), 7.80 (s, 2H), 7.67–7.61 (m, 2H), 7.42–7.33 (m, 2H), 7.25 (dd, 1H, $J = 7.6$, 7.6 Hz), 6.81 (dd, 1H, $J = 7.6$, 7.6 Hz), 5.23 (d, 1H, $J = 8.0$ Hz), 3.90 (s, 9H), 1.51 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 171.9 (d, $J = 42.3$ Hz), 158.9, 147.3, 143.7 (d, $J = 62.7$ Hz), 142.7 (d, $J = 27.0$ Hz), 140.3 (d, $J = 10.3$ Hz), 138.5 (d, $J = 14.6$ Hz), 138.2 (d, $J = 17.5$ Hz), 121.0, 120.8, 120.0, 116.2, 58.0, 39.4, 32.3 (d, $J = 7.2$ Hz); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ 238.8; IR (KBr) 2858, 1738, 1577, 1481, 1442, 1268, 1155, 1029, 775, 731 cm^{-1}; UV (CH_2Cl_2) λ_{max} nm ($\log \varepsilon$) 267 (4.43), 276 (4.47), 366 (4.24), 376 (4.25).

Theoretical Calculation. Molecular orbital calculations were performed using the Gaussian 03 program.[27] Geometry optimizations were done first at the RHF/STO-3G level starting from either the co-ordinates obtained from the crystal structure analyses of **9c**,**d** or co-ordinates modified from those of **9c**,**d**, in the cases of **9a**, **10a**,**c**,**d**,**o**,**p**. The geometries were further optimized at the RHF/6-31+G(d) or RB3LYP/6-31G(d) levels.

Crystal Data for 9b. $C_{31}H_{37}P$, $M_r = 440.61$. Orthorhombic, space group $Pca2_1$ (#29), $a = 16.276(3)$, $b = 9.396(2)$, $c = 16.794(3)$ Å, $V = 2568.4(8)$ Å^3, $Z = 4$, $\rho = 1.139$ g cm^{-3}, $\mu = 1.23$ cm^{-1}; $R_1 = 0.078$ (1766 data, $I > 2\sigma(I)$), $R = 0.179$ (all data), $R_w = 0.180$ (all data), GOF = 2.29. 1854 unique reflections with $2\theta \leq 50.0°$ were recorded on an imaging plate diffractometer (Mo Kα radiation, graphite monochrometer) at −153 °C. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-246318).

Crystal Data for 9c. $C_{28}H_{31}OP$, $M_r = 414.53$. Monoclinic, space group $C2$ (#5), $a = 16.958(4)$, $b = 8.963(6)$, $c = 15.997(3)$ Å, $\beta = 107.98(1)°$, $V = 2312(1)$ Å^3, $Z = 4$, $\rho = 1.190$ g cm^{-3}, $\mu = 1.36$ cm^{-1}; $R_1 = 0.068$ (1953 data, $I > 2\sigma(I)$), $R = 0.175$ (all data), $R_w = 0.171$ (all data), GOF = 3.19. 1966 unique reflections with $2\theta \leq 50.0°$ were recorded on an imaging plate diffractometer (Mo Kα radiation, graphite monochrometer) at −153 °C. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-246319).

Crystal Data for 9d. $C_{29}H_{34}NP$, $M_r = 440.61$. Orthorhombic, space group $Pca2_1$ (#29), $a = 16.323(6)$, $b = 9.415(2)$, $c = 16.117(4)$ Å, $V = 2476(1)$ Å^3, $Z = 4$, $\rho = 1.146$ g cm^{-3}, $\mu =$

1.27 cm^{-1}; $R_1 = 0.059$ (1800 data, $I > 2\sigma(I)$), $R = 0.099$ (all data), $R_w = 0.119$ (all data), GOF = 1.31. 1976 unique reflections with $2\theta \leq 50.0^\circ$ were recorded on an imaging plate diffractometer (Mo Kα radiation, graphite monochrometer) at -120 °C. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-246320).

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