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Preparation and Properties of Fluorenylidene(phenyl)phosphines Bearing Bulky Groups with Electron-Donating Substituents in the Ortho Position on the Phenyl Group

Subaru Kawasaki, Takuma Fujita, Kozo Toyota, and Masaaki Yoshifuji*

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

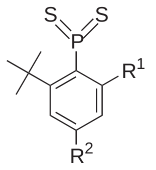
Received September 7, 2004; E-mail: yoshifj@mail.tains.tohoku.ac.jp

Fluorenylidene(phenyl)phosphines having bulky substituents with an electron-donating group in the *o*-position on the phenyl group were prepared and their properties were compared. The prepared materials included 2,4-di-*t*-butyl-6-methoxyphenyl, 2,4-di-*t*-butyl-6-(phenoxymethyl)phenyl, 2,4-di-*t*-butyl-6-(dimethylamino)phenyl, or 2,4-di-*t*-butyl-6-(2-phenylethyl)phenyl. The diphosphenes and dithioxophosphoranes bearing the 2,4-di-*t*-butyl-6-(phenoxymethyl)phenyl group that formed were observed by ^{31}P NMR spectroscopy; the effects of the substituent on these multiply bonded phosphorus species are discussed.

Studies on multiple bonds containing heavier main group elements are of interest in modern element chemistry. Many compounds containing such unusual bonds have been prepared, in many cases, by the aid of kinetic stabilization methodology (so-called steric protection technique).[1] In such sterically protected systems, it is of current interest to study the effect of the introduction of electronically perturbing substituents. Knowledge of the structure–properties relationships in the electronically perturbed sterically protecting systems may lead to designs of novel reagents or materials containing the heavier main-group element with unusual bonding.

Among the studies on the multiply bonded phosphorus compounds,[2] various exotic species such as diphosphenes,[3] phosphacumulenes,[4] phospharadialenes,[5] and dichalcogenoxophosphoranes[6] have been prepared by the use of sterically protecting substituents such as a 2,4,6-tri-*t*-butylphenyl group (abbreviated as Mes*). In the course of our studies on the structure–properties relationships of dithioxophosphoranes **1** (Chart 1),[6,7] we have developed various sterically hindered substituents. We prepared bromobenzene derivatives **2** as precursors of the phosphorus-containing compounds, and have evaluated the effects of their electronically perturbing bulky aryl substituents on **1**.

Research on the structure–properties relationships of other essentially reactive species, such as phosphaethenes, is also important and attractive, because some phosphaethene-based polymers and reagents have recently been reported and further applications are under investigation.[8,9] Polarization of the $-\mathrm{P{=}C}\langle$ bond in phosphaethenes would not be expected to be as large as that of the $-\mathrm{P{=}S}$ bond in dithioxophosphoranes. Thus, in the two different systems, it is interesting to discover how the intramolecular donor-stabilization[7,10] is operating. We report here the preparation and properties of fluorenylidene(phenyl)phosphines **3b–l** with bulky substituents containing electron-donating alkoxy or dialkylamino groups at the *o*-position.[11] The differences between the effects of the *o*-functionalized aryl substituents and those of the *p*-substituted ones are also of interest.



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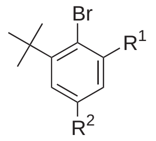

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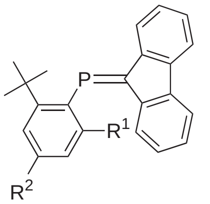

3a: $R^1 = R^2 = t$-Bu
3b: $R^1 = i$-Pr, $R^2 = t$-Bu
3c: $R^1 =$ Me, $R^2 = t$-Bu
3d: $R^1 =$ OMe, $R^2 = t$-Bu
3e: $R^1 = CH_2OMe$, $R^2 = t$-Bu
3f: $R^1 = CH_2OPh$, $R^2 = t$-Bu
3g: $R^1 = CH_2O(4\text{-}t\text{-}BuC_6H_4)$, $R^2 = t$-Bu
3h: $R^1 = CH_2O(4\text{-}MeOC_6H_4)$, $R^2 = t$-Bu
3i: $R^1 = CH_2O$(2-Naphthyl), $R^2 = t$-Bu
3j: $R^1 = NMe_2$, $R^2 = t$-Bu
3k: $R^1 = CH_2NMe_2$, $R^2 = t$-Bu
3l: $R^1 = CH_2CH_2Ph$, $R^2 = t$-Bu
3m: $R^1 = t$-Bu, $R^2 =$ OMe
3n: $R^1 = t$-Bu, $R^2 = NMe_2$

Chart 1.

Results and Discussion

Preparation of Fluorenylidene(phenyl)phosphines.[12] First, fluorenylidene(phenyl)phosphines with bulky substituents containing ethereal groups in the *o*-position on the phenyl group were prepared as follows (Scheme 1). 9-Fluorenyllithium was allowed to react with dichlorophosphine **4d** ($R^1 =$ OMe)[7b] in tetrahydrofuran (THF) at −78 °C to form chloro(fluorenyl)phenylphosphine **5d** (Method A). Treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of molecular sieves MS4A gave fluorenylidene(phenyl)-

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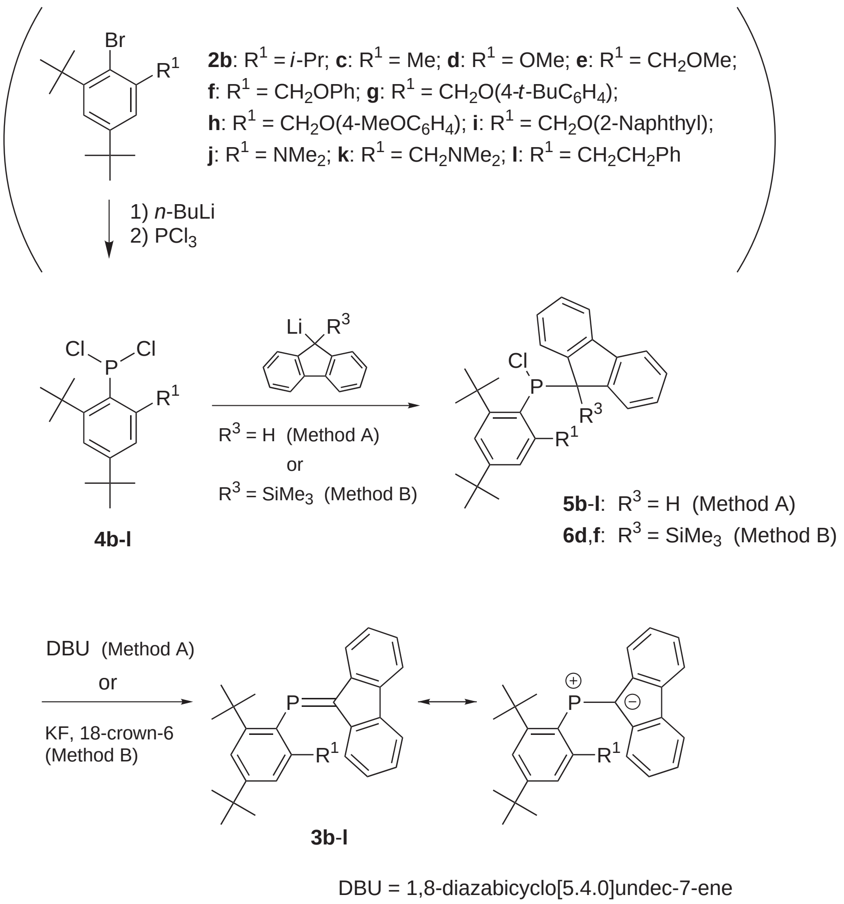


Scheme 1.

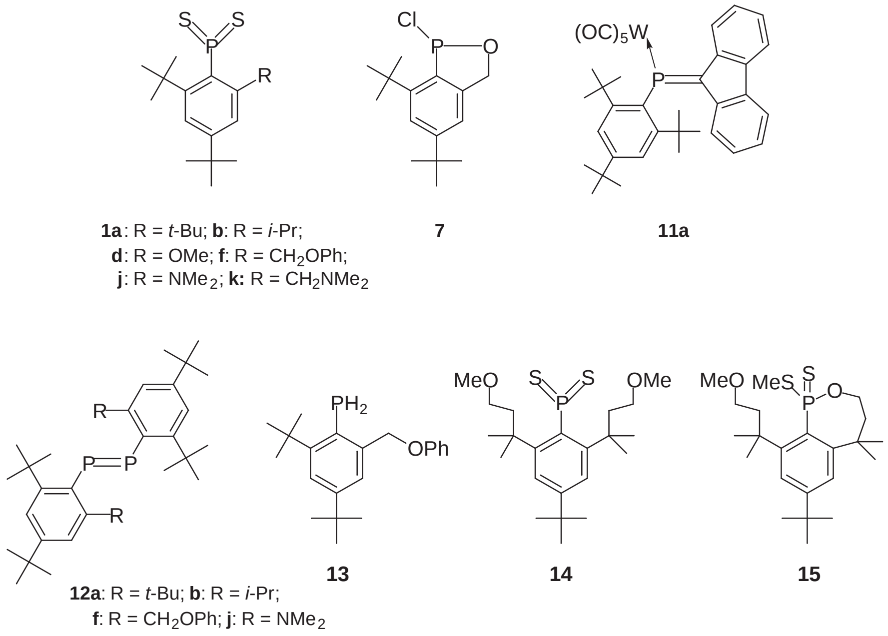
phosphine **3d** in 70% yield. When **4d** was allowed to react with 9-(trimethylsilyl)fluoren-9-yllithium, compound **6d** was obtained (Method B). The attempted conversion of **6d** to **3d** by addition of either KF, TBAF, or Et$_3$N, however, resulted in formation of only a trace amount of **3d** (the major product was the desilylated product **5d**).

Next, the preparation of **3e**, bearing the 2,4-di-*t*-butyl-6-(methoxymethyl)phenyl group, was attempted in a similar manner. Although the formation of a trace amount of **3e** was observed by ^{31}P NMR spectroscopy after the successive treatment of dichlorophosphine **4e** with 9-fluorenyllithium and DBU (Method A), our attempted isolation of **3e** failed due to decomposition. A similar result was obtained in the case of Method B. Moreover, the instability of **4e** seemed to limit its synthetic applications. As we had observed previously,[7c] a cyclization reaction of **4e** occurred[13] at room temperature to give **7** (Chart 2) with elimination of chloromethane (the cyclization was suppressed below 0 °C).

In order to overcome the instability of **4e**, we prepared a 2,6-di-*t*-butyl-6-(phenoxymethyl)phenyl (abbreviated as Phomx: phenoxymethylxylene derivative) congener **4f** as an alternative, as follows (Scheme 2): A mixture of 2-bromo-1-bromomethyl-3,5-di-*t*-butylbenzene (**2o**),[7c] phenol, potassium carbonate, and potassium iodide in DMF was stirred at room temperature for 28 h to give **2f** in 88% yield. When **2f** was treated with butyllithium and water successively, 1,3-di-*t*-butyl-5-(phenoxymethyl)benzene was formed; such formation showed that the halogen–metal exchange reaction had proceeded. The reaction of **2f** with butyllithium, followed by treatment with PCl$_3$, afforded the dichlorophosphine **4f**. This dichlorophosphine is stable at room temperature under an inert atmosphere and the cyclization reaction did not occur. When **4f** was reacted with methanol, compound **8** was obtained in 84% yield without any cyclization product.

The reaction of **4f** with 9-fluorenyllithium gave chloro(fluorenyl)phosphine **5f** (Method A). The treatment of **5f** with DBU formed the corresponding fluorenylidene(phenyl)phosphine **3f**, although an attempted isolation of **3f** from the reaction mixture failed because of a decomposition reaction during the isolation process. However, **3f** was successfully isolated in the reaction of **6f** (Method B) with KF (10 molar amount, see experimental part) in the presence of 18-crown-6 (5 molar amount) in 83% yield based on **2f**, although fluorenylidene(phenyl)phosphine **3f** itself was moisture-sensitive, gradually changing to **9** (Scheme 3).

Furthermore, fluorenylidene(phenyl)phosphines **3j**,**k** with bulky substituents containing an amino functional group in the *o*-position of phenyl were prepared from dichlorophosphines **4j**[7a] and **4k**[7d] (Method A). In these cases, however, the desired fluorenylidene(phenyl)phosphines were highly reactive and they decomposed due to reaction with moisture [MS data of the crude products: **3j**: m/z 427 (M$^+$); **3k** + H$_2$O: m/z 459]. We then tried to prepare [2,4-di-*t*-butyl-6-(2-phenylethyl)phenyl](9-fluorenylidene)phosphine (**3l**), to compare the properties with those of **3f**. Compound **2o** was converted to **10** by a Wittig reaction and then reduced with



1a: R = *t*-Bu; **b**: R = *i*-Pr;
d: R = OMe; **f**: R = CH_2OPh;
j: R = NMe_2; **k:** R = CH_2NMe_2

7

11a

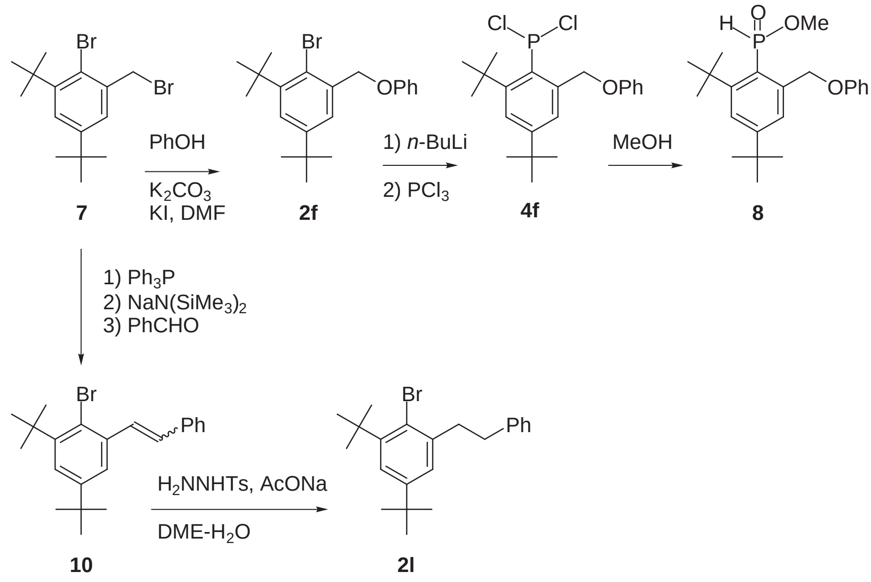
12a: R = *t*-Bu; **b**: R = *i*-Pr;
f: R = CH_2OPh; **j**: R = NMe_2

13

14

15

Chart 2.



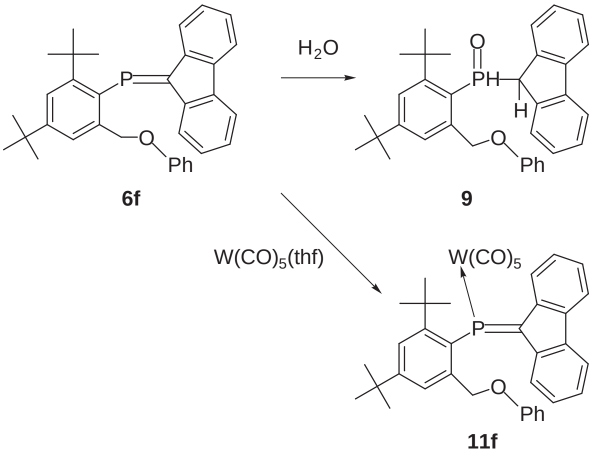
Scheme 2.

diimide[14] to give 2-bromo-1,5-di-*t*-butyl-3-(2-phenylethyl)-benzene (**2l**, Scheme 2). The bromobenzene **2l** was then converted to **3l** via **4l** and **5l** by a method similar to that described above (Method A); however, our attempted isolation of **3l** failed due to its instability. Similarly, our attempted isolation of **3b**,**c** (Method A) by column chromatography failed.

Properties of Fluorenylidene(phenyl)phosphines. Table 1 shows ^{31}P and ^{13}C NMR data of various fluorenylidene(phenyl)phosphines. The ^{31}P NMR signal of **3d** showed a higher-field shift, compared with that of the kinetically stabilized molecule **3a**,[12b] while the chemical shift of **3d** was very close to those of **3e** and **3f**. Although the anisotropic effect of the aromatic ring in **3f** should be taken into account, these facts indicate that the alkoxy group has an electron-donating effect on the phosphorus atom in **3d**–**f**. However, the electron-donating effect in **3d**–**f** is not so strong according to the ^{31}P NMR study. The proximity in chemical shifts of **3d** and **3e** may indicate the contribution of through-space interaction between the oxygen lone pair and the P=C π^* orbital, because through-bond interaction of the oxygen lone pair is not likely effective in the case of **3e**. To gain more precise insight into the effect of the aryloxy group in **3f**, we carried out ^{31}P NMR spectroscopic investigations of the related fluorenylidene(phenyl)phosphines **3g**–**i**. Bromobenzenes **2g**–**i** were prepared from **2o** and converted to **3g**–**i** by similar methods. The ^{31}P chemical shifts of **3g**–**i** were very close to that of **3f** (Table 1). This fact suggests that the interaction between the oxygen atom and the phosphorus atom is not so large and that the perturbation due to the *p*-substituent of the phenoxy group is small. In addition, the instability of **3d–f** suggests that the donor groups in these molecules do not sufficiently stabilize the phosphorus–carbon double bond, while kinetically stabilized **3a** is very stable at room temperature even in air.

Contrary to this, amino-substituted **3k** showed a considerable high-field shift in ^{31}P NMR spectroscopy. This means that the conformationally flexible and electron-donating amino group in **3k** interacted with the phosphorus atom more efficiently than the amino group in **3j** or the methoxy group in **3e**, although the basis for the high reactivity of **3k** is unclear so far.

The *p*-functionalized fluorenylidene(phenyl)phosphines **3m** and **3n** showed a tendency much different from the corresponding *o*-substituted derivatives **3d** and **3j**, respectively. Introduction of the electron-donating group at the *o*-position caused a high-field shift, while introduction in the *p*-position caused a low-field shift compared with **3a**. It is likely that the electron-donating group in the *o*-position mainly affects the π^* orbital of the P=C bond by through-space interaction, causing a high-field shift, while the electron-donating group in the *p*-position seems to affect the nonbonding orbital (mainly the phosphorus lone pair) rather than the P=C π^* orbital, because the bulky aryl π-plane and the P=C π-plane are normally almost perpendicular in the lowest energy conformer (see, for example, X-ray crystallographic results in Ref. 11), leading to a low-field shift.[16]



Scheme 3.

It should be noted that the dimethyl amino group at the para position causes a lower-field shift compared to the methoxy group at the para position. A similar tendency is observed between **3d** and **3j**, probably due to the contribution of through-bond interaction, although the effect is not so large as through-space interaction in these cases, because both **3d** and **3j** showed a net high-field shift, compared to **3a–c**. In the case of **3b**, an inductive effect (through σ bond), which also affects the n orbital, seems to cause a low-field shift compared to **3c**, while a slightly high-field shift of **3a** compared to **3b** may be attributable to steric compression.

Tungsten Carbonyl Complex of Fluorenylidene(phenyl)-phosphine 3f. As mentioned above, among the fluorenylidene(phenyl)phosphines with an *o*-substituent **3b–l**, only **3d** and **3f** were isolated. As **3d** was less stable than **3f** at room temperature, group 6 metal complex formation of **3f** was examined as a representative of **3d** and **3f**, and the results were compared with those of **3a**. When **3f** was treated with [W(CO)$_5$(thf)] in THF at room temperature, a pentacarbonyltungsten complex **11f** [δ_P (CDCl$_3$) = 193.9, satellite, $^1J_{WP}$ = 281.4 Hz] was obtained (the X-ray crystallography of **11f** was reported in a previous communication[11]). Comparison of the ^{31}P NMR data for **11f** with those for **11a** [δ_P (CDCl$_3$) = 215.0, satellite d, $^1J_{WP}$ = 291.2 Hz] shows that the modification in the *o*-substituent affects not only the chemical shift but also the spin–spin coupling ($^1J_{WP}$), which suggests that the trans influence or the trans effect of the complexes is tunable by the *o*-substituent. This may lead to tuning of catalytic ability of appropriate homogeneous catalyst containing sp^2-hybridized phosphorus ligands.[8] It should be noted that the attempted reactions of **3f** with [Cr(CO)$_5$(thf)] or [Mo(CO)$_5$(thf)] under similar conditions failed. It is likely that group 6 metal pentacarbonyls with atomic radii shorter than that of tungsten

Table 1. ^{31}P NMR Data and Selected ^{13}C NMR Data for Fluorenylidene(phenyl)phosphines **3**

Compound	R^1	R^2	$\delta_P$$^{a)}$	$\delta_C$$^{b)}$ (P=*C*) ($^1J_{PC}$/Hz)
a	*t*-Bu	*t*-Bu	256.5$^{c)}$	170.3 (42.7)
b	*i*-Pr	*t*-Bu	257.2	—$^{d)}$
c	Me	*t*-Bu	254.0	—$^{d)}$
d	OMe	*t*-Bu	247.9	171.8 (40.1)$^{e)}$
e	CH$_2$OMe	*t*-Bu	249.7	—$^{d)}$
f	CH$_2$OPh	*t*-Bu	245.8	173.4 (43.1)
g	CH$_2$O(4-*t*-BuC$_6$H$_4$)	*t*-Bu	246.7	172.9 (43.2)
h	CH$_2$O(4-MeOC$_6$H$_4$)	*t*-Bu	246.7	172.8 (43.1)
i	CH$_2$O(2-Naphthyl)	*t*-Bu	245.7	173.3 (43.3)
j	NMe$_2$	*t*-Bu	252$^{f)}$	—$^{d)}$
k	CH$_2$NMe$_2$	*t*-Bu	153$^{f)}$	—$^{d)}$
l	CH$_2$CH$_2$Ph	*t*-Bu	253.9	—$^{d)}$
m	*t*-Bu	OMe	258.0$^{g)}$	171.2 (43.2)
n	*t*-Bu	NMe$_2$	264.8$^{h)}$	171.3 (44.2)

a) In CDCl$_3$, relative to external 85% H$_3$PO$_4$. b) In CDCl$_3$. c) Data taken from Ref. 11. See also, Ref. 12b. d) Attempted purification failed and assignment was unsuccessful. e) Measured in CD$_2$Cl$_2$. f) Measured in THF–C$_6$D$_6$. g) Data taken from Ref. 15. h) Data taken from Ref. 16.

could not coordinate to the phosphorus due to the steric hindrance caused by the *o*-substituents and the conformationally rigid fluorenylidene moiety close to the phosphorus lone pair.

Other Derivatives Bearing the Phomx Group. Furthermore, some ^{31}P NMR spectroscopic investigations of phosphorus compounds containing the Phomx group were carried out. Thus, diphosphene **12f** (Chart 2) was generated from **4f** by addition of magnesium turnings in THF. Dithioxophosphorane **1f** was formed by the reaction of a primary phosphine **13** [δ_P (CDCl$_3$) $= -147.5$, $^1J_{PH} = 205.1$ Hz, prepared by reduction of **4f**] with elemental sulfur in refluxing toluene.

The ^{31}P NMR chemical shift of **12f** [δ_P (C$_6$D$_6$) $= 506.5$, δ_P (CDCl$_3$) $= 506.7$] showed a low-field shift, compared with those of **12a** [δ_P (C$_6$D$_6$) $= 492.4$][3] or **12j** [δ_P (C$_6$D$_6$) $=$ 425.9].[7a] The chemical shift of **12f** is rather close to that of **12b** [δ_P (C$_6$D$_6$) $= 510.5$];[17] thus, the electronic effect of the oxygen atom on the phosphorus–phosphorus double bond in **12f** seems to be small, probably because the P=P bond is not polar in this case, in contrast to the P=C or P=S bonds. The high-field shift of **12a** compared to **12b**,**f** is likely caused by steric compression. As the electronic effect in **12f** now turned out to be relatively small, the reason for the large chemical-shift change in **12j** becomes unclear. One possible reason is the contribution of (*Z*)-form in **12j**;[17] however, further investigation including systematic modification and theoretical calculations for diphosphene derivatives should be carried out. The diphosphene **12f** turned out to be too unstable to be isolated, while **12a** is stable enough to allow isolation in air. This difference in stability is likely caused by steric effects rather than electronic effects.

In contrast, as for the structure–properties relationships of dithioxophosphoranes, the ^{31}P NMR spectrum of **1f** [δ_P (C$_6$D$_6$) $= 264.0$, δ_P (CDCl$_3$) $= 261.3$] showed a significant high-field shift, compared with those of **1a** [δ_P (CDCl$_3$) $=$ 298.2],[6] **1b** [δ_P (CDCl$_3$) $= 291.3$],[17] and **1d** [δ_P (C$_6$D$_6$) $=$ 277.6].[7b] This fact suggests a considerable electron-donating effect of the oxygen lone pairs to the phosphorus center of **1f**, although the effect is not as large as that of **1j** [δ_P (CDCl$_3$) $= 170.6$][7a] or **1k** [δ_P (CDCl$_3$) $= 149.6$].[7d] Compound **1f** was also highly reactive and rapidly decomposed in air. It should be noted that dithioxophosphorane **14** [δ_P (C$_6$D$_6$) $= 295.2$] is not so stable at room temperature due to rearrangement to **15**,[7g] and attempted preparation of **1e** led to the formation of a complex mixture of products, probably via a similar migration of the methyl group.[7f] While **1d** dimerized on concentration of the solution of **1d**,[7b] monomeric **1f** was observed by ^{31}P NMR spectroscopy after concentration and re-solvation. Thus, the Phomx group is a substituent of value as it provides a relatively weak interaction or tuning on the phosphorus center without migration of the phenyl group or polymerization.

Conclusion

In summary, we have evaluated the effects of the Phomx and some related substituents in fluorenylidene(phenyl)phosphines, diphosphenes, and dithioxophosphoranes. Although the effect of the aryloxy group was small in the case of the diphosphene with the non-polar P=P bond, we have observed significant effects in the cases of the dithioxophosphorane and the fluorenylidene(phenyl)phosphine. The degree of interaction turned out to be related to the degree of polarization in the P=X bonds. The ortho-functional groups and the corresponding para-functional groups seem to exert influence in a different manner: The ortho-functional groups seem to affect the π^* orbital, while the para-functional group affect the n orbital. These findings concerning the structure–properties relationships of phosphaethenes will help in the design of new catalysts[8] or polymeric materials[9] containing phosphorus–carbon double bonds. Further studies on the structure–properties relationships of the phosphaethenes and application of the substituents are in progress.

Experimental

Melting points were taken on a Yanagimoto MP-J3 micromelting point apparatus and are uncorrected. ^{1}H NMR spectra, ^{13}C NMR spectra, and ^{31}P NMR spectra were recorded on a Bruker AC-200P or a Bruker Avance-400 spectrometer using CDCl$_3$ as a solvent, unless otherwise specified. In some cases, ^{1}H NMR (600 MHz, CDCl$_3$) spectra and ^{13}C NMR (150 MHz, CDCl$_3$) spectra were obtained on 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. Mass spectra (70 eV) were taken on either a JEOL HX-110 or a Hitachi M-2500S spectrometer. Dichlorophosphines **4b**,[18] **4c**,[19] **4d**,[7b] **4e**,[7c] **4j**,[7a] and **4k**[7d] were prepared according to a previously reported method.

Chloro(2,4-di-*t*-butyl-6-methoxyphenyl)(9-fluorenyl)phosphine (5d). To a solution of fluorene (443 mg, 2.67 mmol) in THF (10 mL) was added 2.7 mmol of butyllithium (1.50 M in hexane, 1 M $=$ 1 mol$\cdot$dm^{-3}) at -78 °C. This solution was added to a solution of **4d** (prepared from 2.67 mmol of **2d**) in THF (15 mL) at -78 °C. The resulting mixture was allowed to warm to ambient temperature and then stirred for 2 h. The solvent was then removed under reduced pressure and a small amount of hexane was added to the residue. Inorganic salt was removed by filtration and the filtrate was concentrated. A small amount of hexane was added and 634 mg (ca. 53% yield) of crude **5d** was obtained by decantation as a colorless solid. **5d**: ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ 83.9; MS (70 eV) *m*/*z* (rel intensity) 452 (M$^+$ + 2; 13), 450 (M$^+$; 34), 414 (M$^+$ − HCl; 16), 285 (MoxPCl$^+$; 100), and 249 (MoxP$^+$ − 1; 63).

Chloro(2,4-di-*t*-butyl-6-methoxyphenyl)[9-(trimethylsilyl)-9-fluorenyl]phosphine (6d). To a solution of 9-(trimethylsilyl)fluorene (467 mg, 1.96 mmol) in THF (20 mL) was added 1.85 mmol of butyllithium (1.42 M in hexane) at -78 °C. This solution was added to a solution of **4d** (prepared from 1.90 mmol of **2d**) in THF (20 mL) at -78 °C and the resulting mixture was allowed to warm to ambient temperature and stirred for 3 h. The solvent was then removed under reduced pressure and a small amount of hexane was added to the residue. Inorganic salt was removed by filtration, and the filtrate was concentrated. Hexane (10 mL) was added and 237 mg (23% yield) of **6d** was obtained by filtration. **6d**: Colorless powder, mp 163–165 °C; ^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ -0.83 (9H, d, $^4J_{PH} = 0.9$ Hz, SiMe$_3$), 1.12 (9H, s, *p*-*t*-Bu), 1.69 (9H, s, *o*-*t*-Bu), 2.40 (3H, s, OMe), 6.00 (1H, d, $J =$ 1.6 Hz, arom.), 6.74 (1H, d, $J = 7.8$ Hz, arom.), 6.84 (1H, m, arom.), 6.94 (1H, dd, $J = 5.4$, 1.7 Hz, arom.), 7.09 (1H, t, $J = 7.5$ Hz, arom.), 7.35–7.37 (2H, m, arom.), 7.74 (1H, d, $J = 7.6$ Hz, arom), 7.87 (1H, m, arom.), and 7.90 (1H, m, arom.); ^{13}C{^{1}H} NMR (150 MHz, CD$_2$Cl$_2$) δ -2.4 (s, SiMe$_3$), 31.4 (s, *p*-C$\underline{\text{Me}}_3$), 34.0 (s, *o*-C$\underline{\text{Me}}_3$), 35.9 (s, *p*-$\underline{\text{C}}$Me$_3$), 38.6 (s, *o*-$\underline{\text{C}}$Me$_3$), 54.1 (s, OMe), 105.3 (s, *m*-arom.), 116.0 (s, *m*-arom.), 119.6 (s, arom., CH), 120.4 (s, arom., CH), 125.4 (s, arom., CH), 125.7 (s, arom., CH), 126.1 (s, arom., CH), 126.9 (s, arom., CH); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 99.8; MS (70 eV) m/z (rel intensity) 524 ($M^+ + 2$; 17), 522 (M^+; 40), 507 ($M^+ -$ Me; 7), 449 ($M^+ -$ Tms; 3), 414 ($M^+ -$ TmsCl; 100), 328 ($M^+ -$ TmsCl − MeO − *t*-Bu + 2; 19), 285 ($MoxPCl^+$; 48), 249 ($MoxP^+ - 1$; 51), 237 ($M^+ -$ MoxPCl; 39), 222 ($C_{13}H_8Tms^+$; 5), 195 ($C_{13}H_8P^+$; 13), 179 ($MoxP^+ -$ *t*-Bu − Me + 1; 10), 165 ($C_{13}H_8^+ + 1$; 23), 73 (Tms^+; 16), and 57 (*t*-Bu^+; 16). Found: m/z 522.2275. Calcd for $C_{31}H_{40}ClOPSi$: M, 522.2275.

(2,4-Di-*t*-butyl-6-methoxyphenyl)(9-fluorenylidene)phosphine (3d) by Method A. To a solution of crude **5d** (264 mg, ca. 0.6 mmol) in THF (3 mL) was added 0.045 mL (0.30 mmol) of DBU in the presence of MS4A. The resulting mixture was stirred for 10 min and the solvent was removed under reduced pressure. To the residue was added a small amount of hexane and the insoluble materials were removed by filtration. The filtrate was concentrated to give 173 mg (ca. 70% yield based on **5d**) of **3d**: Yellow powder, mp 142–145 °C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 1.40 (9H, s, *p-t*-Bu), 1.41 (9H, s, *o-t*-Bu), 3.60 (3H, s, OMe), 6.33 (1H, m), 6.82 (1H, m), 6.89 (1H, d, $J = 1.3$ Hz), 7.19 (1H, m), 7.27–7.33 (3H, m), 7.60 (1H, m), 7.64 (1H, m), and 8.16 (1H, m); ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2) δ 171.8 (d, $^{1}J_{PC} = 40.1$ Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, C_6D_6) δ 246.4; IR (KBr) 1647, 1589, 1442, 1394, 1325, 1207, 1055, 847, 769, and 729 cm^{-1}; MS (70 eV) m/z (rel intensity) 414 (M^+; 100), 249 ($MoxP^+ - 1$; 75), 233 ($MoxP^+ -$ Me − 2; 6), 219 (Mox^+; 5), 193 ($M^+ -$ Mox − 2; 20), 165 ($C_{13}H_9^+$; 42), and 57 (*t*-Bu^+; 20). Found: m/z 414.2115. Calcd for $C_{28}H_{31}OP$: M, 414.2113.

[2,4-Di-*t*-butyl-6-(methoxymethyl)phenyl](9-fluorenylidene)phosphine (3e) by Method B. To a solution of **2e** (375 mg, 1.2 mmol) in THF (4 mL) was added 1.3 mmol of butyllithium (1.50 M solution in hexane) at −78 °C. The resulting solution was added to a solution of PCl_3 (3.7 mmol) in THF (2 mL) at −78 °C. The resulting mixture was allowed to warm to 0 °C and then stirred for 1 h. The solvent and the unreacted PCl_3 were then removed under reduced pressure at 0 °C. The residue was dissolved in THF (4 mL) and a solution of 9-trimethylsilyl-9-fluorenyllithium (1.2 mmol) in THF (8 mL) (prepared from 286 mg of 9-trimethylsilylfluorene and 1.2 mmol of butyllithium) was added at −78 °C. The resulting solution was then allowed to warm to 0 °C and stirred for 30 min. KF (0.7 g, 12 mmol) and 18-crown-6 (1.6 g, 6 mmol) were added and the resulting mixture was allowed to warm to ambient temperature. An aliquot of the solution was analyzed by ^{31}P NMR spectroscopy, which indicated formation of **3e**. The solvent was then removed under reduced pressure, 20 mL of anhydrous hexane was added, and undissolved inorganic salt was filtered off. Solvent of the filtrate was removed under reduced pressure and the residue was quickly analyzed by ^{31}P NMR spectroscopy. Although the measurement revealed that a signal due to **3e** appeared at $\delta = 249.7$ in $CDCl_3$, the residue was a complex mixture of products. The attempted isolation of **3e** was unsuccessful [silica-gel column chromatography, recrystallization, and recycling GPC (gel permeation column chromatography) were used]. A trapping experiment using MeOH gave a more complicated mixture of products.

2-Bromo-1,5-di-*t*-butyl-3-(phenoxymethyl)benzene (2f) and the Related Bromobenzenes (2g–i). 2-Bromo-1-bromomethyl-3,5-di-*t*-butylbenzene (**2o**, 5.00 g, 13.8 mmol), phenol (1.53 g, 16.3 mmol), potassium carbonate (3.13 g, 22.7 mmol), and potassium iodide (0.26 g, 1.5 mmol) were placed in a 100 mL flask. To this mixture was added *N*,*N*-dimethylformamide (30 mL) and the resulting mixture was stirred at room temperature for 28 h. The reaction mixture was then diluted with diethyl ether and the organic phase was successively washed with water and brine, and dried over $MgSO_4$. The solvent was removed and the residue was recrystallized from hexane–MeOH (20:1) to give 4.40 g (88% yield) of **2f**. Bromobenzenes **2g**–**i** were prepared in a similar manner.

2f: Colorless powder, mp 62–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (9H, s, *p-t*-Bu), 1.63 (9H, s, *o-t*-Bu), 5.22 (2H, s, CH_2O), 7.05 (2H, d, $J = 7.5$ Hz), 7.10 (1H, t, $J = 8.7$ Hz), 7.38 (2H, dd, $J = 8.7$, 7.5 Hz), 7.53 (1H, d, $J = 2.4$ Hz), and 7.55 (1H, d, $J = 2.4$ Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 30.6 (p-C$\underline{\mathrm{Me}}_3$), 31.7 ($o$-C$\underline{\mathrm{Me}}_3$), 35.3 ($p$-$\underline{\mathrm{C}}Me_3$), 37.8 ($o$-$\underline{\mathrm{C}}Me_3$), 71.6 ($CH_2O$), 115.5 (arom.), 120.6 (arom.), 121.5 (arom.), 124.7 (arom.), 125.2 (arom.), 129.9 (arom.), 137.7 (arom.), 147.9 (arom.), 150.1 (arom.), and 159.2 (arom.); IR (KBr) 1595, 1495, 1471, 1427, 1387, 1365, 1265, 1174, 1080, 1020, 885, 835, 750, and 692 cm^{-1}; MS (70 eV) m/z (rel intensity) 376 ($M^+ + 2$; 10), 374 (M^+; 10), 283 ($M^+ -$ OPh + 2; 75), 281 ($M^+ -$ OPh; 76), 187 ($M^+ -$ Br − CH_2OPh + 1; 6), and 57 (*t*-Bu^+; 100). Found: m/z 374.1247. Calcd for $C_{21}H_{27}BrO$: M, 374.1245.

2g: Colorless solid, mp 73–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (9H, s, *t*-Bu), 1.33 (9H, s, *t*-Bu), 1.59 (9H, s, *o-t*-Bu), 5.16 (2H, s, CH_2O), 6.99 (2H, d, $J = 8.8$ Hz), 7.35 (2H, d, $J = 8.8$ Hz), and 7.48 (2H, br. s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 30.5 (C$\underline{\mathrm{Me}}_3$), 31.7 (C$\underline{\mathrm{Me}}_3$), 31.9 (C$\underline{\mathrm{Me}}_3$), 35.2 ($p$-$\underline{\mathrm{C}}Me_3$), 37.8 ($o$-$\underline{\mathrm{C}}Me_3$), 71.8 ($CH_2O$), 114.9 (arom.), 120.7 (arom.), 124.8 (arom.), 125.2 (arom.), 126.7 (arom.), 137.9 (arom.), 144.1 (arom.), 147.9 (arom.), 150.1 (arom.), and 156.9 (arom.); IR (KBr) 1606, 1512, 1363, 1242, 1182, 1022, and 825 cm^{-1}; MS (70 eV) m/z (rel intensity) 432 ($M^+ + 2$; 19), 430 (M^+; 19), 283 ($M^+ -$ OAr + 2; 96), 281 ($M^+ -$ OAr; 100), and 57 (*t*-Bu^+; 83).

2h: Colorless solid, mp 109–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (9H, s, *p-t*-Bu), 1.62 (9H, s, *o-t*-Bu), 4.00 (3H, s, MeO), 5.16 (2H, s, CH_2O), 6.90 (2H, d, $J = 9.1$ Hz), 7.01 (2H, d, $J = 9.1$ Hz), 7.51 (2H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 30.6 (p-C$\underline{\mathrm{Me}}_3$), 31.7 ($o$-C$\underline{\mathrm{Me}}_3$), 35.2 ($p$-$\underline{\mathrm{C}}Me_3$), 37.8 ($o$-$\underline{\mathrm{C}}Me_3$), 56.1 (MeO), 72.5 ($CH_2O$), 115.1 (arom.), 116.5 (arom.), 120.5 (arom.), 124.6 (arom.), 125.2 (arom.), 138.0 (arom.), 147.9 (arom.), 150.1 (arom.), 153.4 (arom.), and 154.5 (arom.); IR (KBr) 1593, 1510, 1369, 1238, 1065, and 820 cm^{-1}; MS (70 eV) m/z (rel intensity) 406 ($M^+ + 2$; 14), 404 (M^+; 14), 283 ($M^+ -$ OAr + 2; 51), 281 ($M^+ -$ OAr; 52), and 57 (*t*-Bu^+; 100). Found: m/z 404.1340. Calcd for $C_{22}H_{29}BrO_2$: M, 404.1351.

2i: Colorless solid, mp 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (9H, s, *p-t*-Bu), 1.64 (9H, s, *o-t*-Bu), 5.33 (2H, s, CH_2O), 7.2–7.6 (6H, m), and 7.7–7.9 (3H, m); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 30.6 (p-C$\underline{\mathrm{Me}}_3$), 31.7 ($o$-C$\underline{\mathrm{Me}}_3$), 35.3 ($p$-$\underline{\mathrm{C}}Me_3$), 37.8 ($o$-$\underline{\mathrm{C}}Me_3$), 71.7 ($CH_2O$), 107.9 (arom.), 119.5 (arom.), 120.8 (arom.), 124.1 (arom.), 124.8 (arom.), 125.4 (arom.), 126.8 (arom.), 127.3 (arom.), 128.1 (arom.), 129.6 (arom.), 129.9 (arom.), 135.0 (arom.), 137.6 (arom.), 148.0 (arom.), 150.2 (arom.), and 157.1 (arom.); IR (KBr) 1628, 1599, 1512, 1464, 1396, 1380, 1363, 1254, 1213, 1178, 1117, 1007, 883, 839, 812, and 744 cm^{-1}; MS (70 eV) m/z (rel intensity) 426 ($M^+ + 2$; 9), 424 (M^+; 10), 345 ($M^+ -$ Br; 16), 283 ($M^+ -$ ONaph + 2; 31), 281 ($M^+ -$ ONaph; 30), 115 ($M^+ -$ Br − CH_2ONaph − *t*-Bu − Me − 1; 100), and 57 (*t*-Bu^+; 87). Found: m/z 424.1403. Calcd for $C_{25}H_{29}BrO$: M, 424.1402.

Methyl [2,4-Di-*t*-butyl-6-(phenoxymethyl)phenyl]phosphinate (8). Bromobenzene **2f** (103 mg, 0.27 mmol) in THF (1 mL) was lithiated with 0.31 mmol of butyllithium (1.58 M in hexane) at −78 °C; the resulting solution was then added to a THF (0.5 mL) solution of phosphorus trichloride (1.15 mmol) at that temperature. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. The solvent and the unreacted PCl_3 were removed under reduced pressure to give **4f**. MeOH (2 mL) was added to the residue and the resulting mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2/hexane–EtOAc) to give **8** (85 mg, 84% yield).

4f: Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (9H, s, *p*-*t*-Bu), 1.63 (9H, d, $^4J_{PH} = 1.2$ Hz, *o*-*t*-Bu), 5.79 (2H, s, CH_2O), 7.00 (1H, tt, $^3J_{HH} = 7.3$ Hz and $^4J_{HH} < 1$ Hz, *p*-Ph), 7.07 (2H, dd, $^3J_{HH} = 8.5$ Hz and $^4J_{HH} < 1$ Hz, *o*-Ph), 7.34 (2H, dd, $^3J_{HH} = 8.5$ Hz and $^3J_{HH} = 7.3$ Hz, *m*-Ph), 7.49 (1H, dd, $^4J_{PH} = 6.6$ Hz and $^4J_{HH} = 1.9$ Hz, *m*-Phomx), and 7.78 (1H, d, $^4J_{HH} = 1.9$ Hz, *m*-Phomx.); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 31.4 (s, *p*-C$\underline{Me}_3$), 34.5 (d, $^4J_{PC} = 23.5$ Hz, *o*-C$\underline{Me}_3$), 35.8 (s, *p*-$\underline{C}Me_3$), 38.0 (s, *o*-$\underline{C}Me_3$), 67.8 (s, CH_2O), 115.5 (s, arom. CH), 121.4 (s, arom. CH), 123.0 (d, $^3J_{PC} = 9.0$ Hz, *m*-Phomx), 126.5 (s, arom. CH), 130.0 (arom. CH), 133.0 (d, $^1J_{PC} = 83.7$ Hz, *ipso*-Phomx), 144.9 (s, *p*-Phomx), 155.1 (d, $^2J_{PC} = 33.8$ Hz, *o*-Phomx), 155.9 (s, *o*-Phomx), and 159.1 (s, *ipso*-Ph); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 162.3; MS (70 eV) *m*/*z* (rel intensity) 400 ($M^+ + 4$; 0.3), 398 ($M^+ + 2$; 1), 396 (M^+; 2), 361 ($M^+ - Cl$; 17), and 303 ($M^+ - OPh$; 100). Found: *m*/*z* 396.1204. Calcd for $C_{21}H_{27}Cl_2OP$: M, 396.1177. The melting point value was ambiguous because thermal decomposition occurred on heating.

8: Colorless crystals, mp 77–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (9H, s, *p*-*t*-Bu), 1.57 (9H, s, *o*-*t*-Bu), 3.84 (3H, d, $^3J_{PH} = 12.3$ Hz, OMe), 5.51 (1H, d, $^2J_{HH} = 13.0$ Hz, C$\underline{H}$H′O), 5.61 (1H, d, $^2J_{HH} = 13.0$ Hz, CH$\underline{H'}$O), 6.97 (1H, t, $J = 7.5$ Hz), 7.05 (2H, d, $J = 8.6$ Hz), 7.30 (2H, dd, $J = 8.6, 7.5$ Hz), 7.51 (1H, d, $J = 6.0$ Hz), 7.64 (1H, s), and 8.46 (1H, d, $^1J_{PH} = 569.4$ Hz, PH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 31.4 (s, *p*-C$\underline{Me}_3$), 34.1 (s, *o*-C$\underline{Me}_3$), 35.6 (s, *p*-$\underline{C}Me_3$), 37.2 (d, $^3J_{PC} = 2.6$ Hz, *o*-$\underline{C}Me_3$), 53.8 (d, $^2J_{PC} = 6.1$ Hz, OMe), 68.5 (d, $^3J_{PC} = 6.4$ Hz, CH_2O), 115.4 (s, *o*-Ph), 121.2 (s, *p*-Ph), 123.3 (d, $^3J_{PC} = 13.4$ Hz, *m*-Phomx), 124.4 (d, $^3J_{PC} = 126.9$ Hz, *ipso*-Phomx), 125.0 (d, $^3J_{PC} = 10.7$ Hz, *m*-Phomx), 129.9 (s, *m*-Ph), 143.0 (d, $^2J_{PC} = 4.9$ Hz, *o*-Phomx), 153.4 (d, $^2J_{PC} = 12.3$ Hz, *o*-Phomx), 155.4 (d, $^4J_{PC} = 2.3$ Hz, *p*-Phomx), and 159.0 (s, *ipso*-Ph); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9 (d, $^1J_{PH} = 569.6$ Hz); IR (NaCl) 3060–2870 (br.), 2431, 1727, 1600, 1546, 1496, 1402, 1375, 1240, 1220, 1010, 883, 855, 838, 790, and 692 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 374 (M^+; 8), 356 ($M^+ - O - H - 1$; 11), and 281 ($M^+ - OPh$; 100). Found: *m*/*z* 374.2008. Calcd for $C_{22}H_{31}O_3P$: M, 374.2011.

1,3-Di-*t*-butyl-5-(phenoxymethyl)benzene. Compound **2f** (192 mg, 0.51 mmol) in THF (2 mL) was lithiated with 1.7 mmol of butyllithium (1.57 M in hexane) at −78 °C. To the solution was added 1 mL of water. The resulting mixture was stirred at that temperature for 10 min, and then allowed to warm to room temperature. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography (SiO_2/hexane) to give 114 mg (75%) of 1,3-di-*t*-butyl-5-(phenoxymethyl)benzene: Colorless crystals, mp 53–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (18H, s, *t*-Bu), 5.05 (2H, s, CH_2O), 6.99 (1H, t, $J = 7.6$ Hz), 7.04 (2H, dd, $J = 8.8, 1.2$ Hz), 7.30–7.35 (4H, m), and 7.43 (1H, t, $J = 1.8$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 31.9 (C$\underline{Me}_3$), 35.3 (C$\underline{Me}_3$), 71.2 (CH_2O), 115.2 (*o*-Ph), 116.6 (arom.), 121.2 (*p*-Ph), 122.7 (arom.), 129.8 (*m*-Ph), 136.3 (arom.), 151.5 (arom.), and 159.5 (*ipso*-Ph); IR (KBr) 1599, 1494, 1473, 1367, 1295, 1238, 1172, 1081, 1014, 879, 829, 752, 713, and 692 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 297 ($M^+ + 1$; 100). Found: *m*/*z* 296.2132. Calcd for $C_{21}H_{28}O$: M, 296.2140.

[2,4-Di-*t*-butyl-6-(phenoxymethyl)phenyl](9-fluorenylidene)phosphine (3f) by Method B. A freshly prepared solution of (9-trimethylsilyl-9-fluorenyl)lithium [prepared from 138 mg (0.58 mmol) of 9-trimethylsilylfluorene and 1.1 molar amount of butyllithium in THF (1 mL) at 0 °C] was added dropwise to a THF (1 mL) solution of **4f** [prepared from 200 mg (0.53 mmol) of **2f** by the method described above; the unreacted PCl_3 was removed under reduced pressure] at −78 °C. The resulting solution of **6f** was stirred at 0 °C for 30 min. To the solution were added KF (370 mg, 6.37 mmol) and 18-crown-6 (621 mg, 2.35 mmol) and the resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure; hexane (50 mL) was added to the residue, the mixture was filtered, and the filtrate was concentrated under reduced pressure. Column chromatography of the residue provided 215 mg (83% yield) of **3f**. When KF (1 molar amount) and 18-crown-6 (1 molar amount) was used, the reaction proceeded very slowly and **3f** decomposed before consumption of **6f**. Moreover, when KF and 18-crown-6 were used in 1:1 ratio, separation of **3f** from the reaction mixture became troublesome.

6f: $^{31}P\{^1H\}$ NMR (162 MHz, THF–C_6D_6) δ 95.8.

3f: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (9H, s, *p*-*t*-Bu), 1.54 (9H, s, *o*-*t*-Bu), 4.82 (1H, d, $^2J_{HH} = 12.7$ Hz, C$\underline{H}$HO), 5.30 (1H, d, $^2J_{HH} = 12.7$ Hz, CH$\underline{H}$O), 6.10 (1H, dd, $J = 8.0, 2.6$ Hz), 6.8–6.9 (4H, m), 7.16 (2H, m), 7.25 (2H, d, $J = 7.5$ Hz), 7.35 (2H, dd, $J = 7.5, 7.5$ Hz), 7.56 (1H, d, $J = 1.6$ Hz), 7.63 (2H, dd, $J = 8.0, 8.0$ Hz), 7.68 (1H, br. s), and 8.14 (1H, dd, $J = 8.0, 7.5$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 31.9 (s, *p*-C$\underline{Me}_3$), 32.0 (d, $^4J_{PC} = 5.7$ Hz, *o*-C$\underline{Me}_3$), 35.6 (s, *p*-$\underline{C}Me_3$), 38.1 (s, *o*-$\underline{C}Me_3$), 70.5 (d, $^3J_{PC} = 9.1$ Hz, CH_2O), 115.5 (s, Ph), 119.8 (s, arom. CH), 119.9 (s, arom. CH), 121.2 (d, $^3J_{PC} = 22.8$ Hz, *m*-Phomx), 121.4 (s, arom. CH), 124.1 (s, arom. CH), 124.2 (s, arom. CH), 126.2 (d, $J_{PC} = 7.7$ Hz, arom. CH), 127.6 (d, $^3J_{PC} = 3.2$ Hz, *m*-Phomx), 127.7 (d, $J_{PC} = 2.3$ Hz, arom. CH), 129.1 (d, $J_{PC} = 6.6$ Hz, arom. CH), 129.4 (d, $J_{PC} = 6.1$ Hz, arom. CH), 129.8 (s, arom. *m*-Ph), 134.0 (d, $^1J_{PC} = 52.7$ Hz, *ipso*-Phomx), 138.4 (d, $J_{PC} = 14.0$ Hz, Flu), 138.9 (d, $J_{PC} = 17.2$ Hz, Flu), 140.1 (s, *o*-Phomx), 140.3 (d, $J_{PC} = 10.2$ Hz, Flu), 143.2 (d, $J_{PC} = 25.6$ Hz, Flu), 153.2 (s, *p*-Phomx), 154.3 (d, $^2J_{PC} = 2.9$ Hz, *o*-Phomx), 159.0 (s, *ipso*-Ph), and 173.4 (d, $^1J_{PC} = 43.1$ Hz, P=$\underline{C}$); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 245.8; UV (hexane) 256 ($\log \varepsilon$ 4.24), 266 (4.33), 275 (4.38), and 365 nm (4.08); IR (NaCl) 1722, 1597, 1492, 1444, 1365, 1295, 1234, 1172, 1033, 883, 759, and 690 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 490 (M^+; 65), 397 ($M^+ - OPh$; 100), 383 ($M^+ - CH_2OPh$; 34), 341 ($M^+ - OPh - t\text{-Bu} + 1$; 41), 165 ($C_{13}H_9^+$; 32), 149 (84), and 57 ($t\text{-Bu}^+$; 86). Found: *m*/*z* 490.2432. Calcd for $C_{34}H_{35}OP$: M, 490.2426.

[2,4-Di-*t*-butyl-6-(phenoxymethyl)phenyl](9-fluorenyl)phosphine Oxide (9) by Method A. A freshly prepared solution of 9-fluorenyllithium [prepared from 148 mg (0.89 mmol) of fluorene and 1.1 molar amount of butyllithium in THF (1 mL)] was added dropwise to a THF (3 mL) solution of **4f** [prepared from 300 mg (0.80 mmol) of **2f** by the method described above; the unreacted PCl_3 was removed in vacuo] at −78 °C. The resulting solution of **5f** was stirred at 0 °C for 10 min. To the solution was added DBU (0.14 mL, 0.99 mmol) and the resulting mixture was stirred at 0 °C for 30 min and then allowed to warm to room temperature. The ^{31}P NMR spectrum of the solution showed a signal due to **3f**. The solvent was then removed under reduced pressure, and hexane (30 mL) was added to the residue; the mixture was filtered, and the filtrate was concentrated under reduced pressure. ^{31}P NMR spectrum of the residue showed that **3f** decomposed to **9**, which was isolated (169 mg, 42% yield) by recycling gel permeation chromatography (Japan Analytical Industry, JAIGEL H1+H2 column, eluent: $CHCl_3$).

5f: Colorless powder, mp 179–182 °C, $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 82.2; MS m/z (rel intensity) 528 ($M^+ + 2$; 0.8), 526 (M^+; 2), 490 ($M^+ - HCl$; 5), 397 ($M^+ - HCl - OPh$; 10), 325 ($M^+ - Cl - C_{13}H_9 - 1$; 68), and 165 ($C_{13}H_9{}^+$; 100). Found: m/z 526.2175. Calcd for $C_{34}H_{36}ClOP$: M, 526.2192.

9: Colorless powder, mp 206–208 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (9H, s, *p*-*t*-Bu), 1.43 (9H, s, *o*-*t*-Bu), 4.95 (1H, dd, $^2J_{PH} = 24.5$ Hz, $^3J_{HH} = 7.0$ Hz, P–CH), 5.35 (1H, d, $^2J_{HH} = 11.3$ Hz, $C\underline{H}H'O$), 6.25 (1H, d, $J = 7.5$ Hz), 6.41 (1H, d, $^2J_{HH} = 11.3$ Hz, $CH\underline{H'}O$), 6.91 (1H, dd, $J = 7.5$, 7.5 Hz), 6.98 (1H, t, $J = 7.3$ Hz), 7.08 (1H, dd, $^1J_{PH} = 502.6$ Hz and $^3J_{HH} = 7.0$ Hz, PH), 7.10 (2H, d, $J = 8.0$ Hz), 7.26–7.31 (1H, m), 7.30 (2H, dd, $J = 8.0$, 7.3 Hz), 7.40 (1H, dd, $J = 7.5$, 7.5 Hz), 7.47 (1H, dd, $J = 7.5$, 7.5 Hz), 7.55 (1H, d, $J = 4.5$ Hz), 7.69 (1H, s), 7.73 (1H, d, $J = 7.5$ Hz), 7.81 (1H, d, $J = 7.5$ Hz), and 8.05 (1H, d, $J = 7.5$ Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 31.0 (s, *p*-$C\underline{Me}_3$), 33.0 (s, *o*-$C\underline{Me}_3$), 35.2 (s, *p*-$\underline{C}Me_3$), 36.8 (s, *o*-$\underline{C}Me_3$), 50.8 (d, $^1J_{PC} = 56.3$ Hz, P(O)–CH), 68.5 (d, $^3J_{PC} = 6.0$ Hz, CH_2O), 114.9 (s, *o*-Ph), 119.9 (s, arom. CH), 120.1 (s, arom. CH), 121.4 (s, *p*-Ph), 124.0 (d, $^3J_{PC} = 11.4$ Hz, *m*-Phomx), 126.5 (d, $J_{PC} = 2.9$ Hz, arom. CH), 126.6 (d, $J_{PC} = 2.9$ Hz, arom. CH), 127.3 (d, $J_{PC} = 3.4$ Hz, arom. CH), 127.4 (s, *m*-Phomx), 127.4 (d, $J_{PC} = 2.9$ Hz, arom. CH), 127.9 (d, $J_{PC} = 2.3$ Hz, arom. CH), 128.0 (d, $J_{PC} = 1.6$ Hz, arom. CH), 129.5 (d, $^1J_{PC} = 72.1$ Hz, *ipso*-Phomx), 129.6 (s, arom. *m*-Ph), 137.3 (s, *o*-Phomx), 140.8 (d, $J_{PC} = 4.0$ Hz, Flu), 141.0 (d, $J_{PC} = 4.5$ Hz, Flu), 141.9 (d, $J_{PC} = 6.9$ Hz, Flu), 142.1 (d, $J_{PC} = 5.1$ Hz, Flu), 153.8 (d, $^2J_{PC} = 8.6$ Hz, *o*-Phomx), 155.3 (d, $^4J_{PC} = 2.3$ Hz, *p*-Phomx), and 158.3 (s, *ipso*-Ph); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8 (dd, $^1J_{PH} = 502.6$ Hz and $^2J_{PH} = 24.5$ Hz); IR (KBr) 3133, 2998, 1596, 1485, 1448, 1230, 1180, 1008, 800, and 748 cm^{-1}; MS (70 eV) m/z (rel intensity) 508 (M^+; 10), 415 ($M^+ - OPh$; 13), 343 ($M^+ - C_{13}H_9$; 51), 325 ($M^+ - C_{13}H_{10} - OH$; 11), 249 ($M^+ - C_{13}H_{10} - OPh$; 42), and 165 ($C_{13}H_9{}^+$; 100). Found: m/z 508.2502. Calcd for $C_{34}H_{37}O_2P$: M, 508.2531.

2-Bromo-1,5-di-*t*-butyl-3-(2-phenylethyl)benzene (2l). A mixture of **7** (3.1 g, 8.56 mmol) and triphenylphosphine (2.4 g, 9.16 mmol) in toluene (20 mL) was stirred at 90 °C for 3 h. The mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. To the residue was added THF (40 mL), and then were added 10 mmol of sodium bis(trimethylsilyl)amide (1 M solution in THF) and benzaldehyde (1 mL, 9.84 mmol) at 0 °C; the resulting solution was stirred at room temperature for 4 h. The solution was then worked up using Et_2O and brine; the organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO_2) of the residue provided 1.3 g (41% yield) of **10**. Compound **10** (490 mg, 1.32 mmol) was then dissolved in 1,2-dimethoxyethane (35 mL) and *p*-tolylsulfonylhydrazide (3.0 g, 16.1 mmol) was added. The resulting solution was refluxed and aqueous NaOAc (1.4 g in 7 mL of water) was slowly added. The resulting mixture was refluxed for an additional 1 h and then allowed to cool to room temperature. Again, *p*-tolylsulfonylhydrazide (3.0 g, 16.1 mmol) was added and the solution was refluxed, and aqueous NaOAc (1.4 g in 7 mL of water) was slowly added. After being cooled to room temperature, the solution was worked up using Et_2O, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO_2) of the residue provided 488 mg (99% yield) of **2l**: Colorless solid, mp 37–39 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (9H, s, *p*-*t*-Bu), 1.62 (9H, s, *o*-*t*-Bu), 3.16 (2H, m, CH_2), 3.77 (2H, m, CH_2), 7.05 (1H, d, $J = 2.5$ Hz), 7.2–7.4 (5H, m), and 7.40 (1H, d, $J = 2.5$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 30.7 (*p*-$C\underline{Me}_3$), 31.7 (*o*-$C\underline{Me}_3$), 35.0 (*p*-$\underline{C}Me_3$), 36.9 (*o*-$\underline{C}Me_3$), 37.9 (CH_2), 41.0 (CH_2), 122.4 (arom., CBr), 123.8 (arom., CH), 126.2 (arom., CH), 126.3 (arom., CH), 128.8 (Ph), 129.0 (Ph), 142.4 (arom.), 142.5 (arom.), 148.0 (arom.), and 149.7 (arom.); IR (KBr) 1454, 1394, 1362, 1014, and 696 cm^{-1}; MS (70 eV) m/z (rel intensity) 374 ($M^+ + 2$; 58), 372 (M^+; 73), 359 ($M^+ - Me + 2$; 40), 357 ($M^+ - Me$; 46), 283 ($M^+ - CH_2Ph + 2$; 76), 281 ($M^+ - CH_2Ph$; 78), 91 ($PhCH_2{}^+$; 28), and 57 (t-Bu^+; 100).

^{31}P NMR Spectroscopic Observation of 3b, 3c, and 3g–l. Typical Procedure (Method A): To a solution of **2** (1.5 mmol) in THF (17 mL) was added 1.6 mmol of butyllithium (hexane solution) at −78 °C. The resulting mixture was stirred for 10 min and then was added to a THF (17 mL) solution of PCl_3 (3.9 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and then stirred for 1 h. The solvent and the unreacted PCl_3 were removed under reduced pressure and then THF (18 mL) was added to the residue. In a separate flask, 0.36 g (2.2 mmol) of fluorene in THF (17 mL) was treated with butyllithium (2.4 mmol) at −78 °C. The resulting solution of 9-fluorenyllithium was stirred for 10 min and then added to the THF solution of **4** at −78 °C. The reaction mixture was stirred for 90 min. ^{31}P NMR spectroscopic monitoring of the mixture showed a signal due to **5**. To the resulting solution was added 2.0 mmol of DBU. The solution was then stirred for 1 h. ^{31}P NMR spectroscopic monitoring of the mixture showed a signal due to **3** (Table 1); however, attempted isolation of **3** by column chromatography (Al_2O_3) or by recrystallization failed due to decomposition of the desired product. $^{31}P\{^1H\}$ NMR (162 MHz) data: **4l**, δ (THF–C_6D_6) 166; **5b**, δ (THF–C_6D_6) 83; **5j**, δ (THF–C_6D_6) 83; **5k**, δ (THF–C_6D_6) 86; **5i**, δ (C_6D_6) 85.6.

Pentacarbonyl{[2,4-di-*t*-butyl-6-(phenoxymethyl)phenyl](9-fluorenylidene)phosphine}tungsten (11f). A solution of $[W(CO)_5(thf)]$ [prepared from 160 mg, 0.45 mmol of $[W(CO)_6]$ in THF (20 mL)] was added to **3f** (72 mg, 0.15 mmol). The resulting mixture was stirred at room temperature for 3 days and then the solvent was removed under reduced pressure. Column chromatography of the residue (SiO_2, hexane–toluene 20:1) provided 26 mg (28% yield) of **11f**: Orange prisms, mp 167 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (9H, s, *p*-*t*-Bu), 1.57 (9H, s, *o*-*t*-Bu), 5.17 (1H, dd, $^2J_{HH} = 12.3$ Hz and $^4J_{PH} = 1.6$ Hz, $C\underline{H}H'O$), 5.52 (1H, dd, $^2J_{HH} = 12.3$ Hz and $^4J_{PH} = 2.2$ Hz, $CH\underline{H'}O$), 6.44 (1H, dd, $J = 8.0$, 3.6 Hz), 6.64–6.66 (2H, m), 6.83–6.90 (2H, m), 7.08–7.11 (2H, m), 7.24 (1H, ddd, $J = 7.4$, 7.4, 2.4 Hz), 7.34 (1H, dd, $J = 7.8$, 7.8 Hz), 7.41 (1H, ddd, $J = 7.4$, 7.4, 2.0 Hz), 7.62 (1H, d, $J = 7.2$ Hz), 7.67 (1H, d, $J = 7.6$ Hz), 7.72–7.78 (2H, m), and 8.69 (1H, dd, $J = 7.6$, 4.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 69.7 (d, $^3J_{PC} = 8.6$ Hz, CH_2O), 168.2 (d, $^1J_{PC} = 40.4$ Hz, $P{=}\underline{C}$), 195.9 (d, $^2J_{PC} = 9.6$ Hz, satellite $^1J_{WC} = 125.7$ Hz, CO_{eq}), and 198.8 (d, $^2J_{PC} = 31.7$ Hz, CO_{ax}); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 193.9 (satellite, $^1J_{WP} = 281.4$ Hz); UV (hexane) 211 ($\log\varepsilon$ 4.90), 337 (3.88), and 474 nm (4.38); IR (KBr) 2071, 1957, 1919, 1597, and 1232 cm^{-1}; MS (70 eV) m/z (rel intensity) 814 (M$^+$; 6), 730 (M$^+$ − 3CO; 8), 674 (M$^+$ − 5CO; 8), 490 (M$^+$ − W(CO)$_5$; 42), 397 (M$^+$ − OPh − W(CO)$_5$; 63), 341 (M$^+$ − *t*-Bu − OPh − W(CO)$_5$; 23), 165 (Flu$^+$ + 1; 34), 57 (*t*-Bu$^+$; 89), and 28 (CO$^+$; 100).

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