



# Preparation and properties of fluorenylidene phosphines bearing an electron-donating substituent, 2-alkoxy-4,6-di-*t*-butylphenyl or 2-(alkoxymethyl)-4,6-di-*t*-butylphenyl

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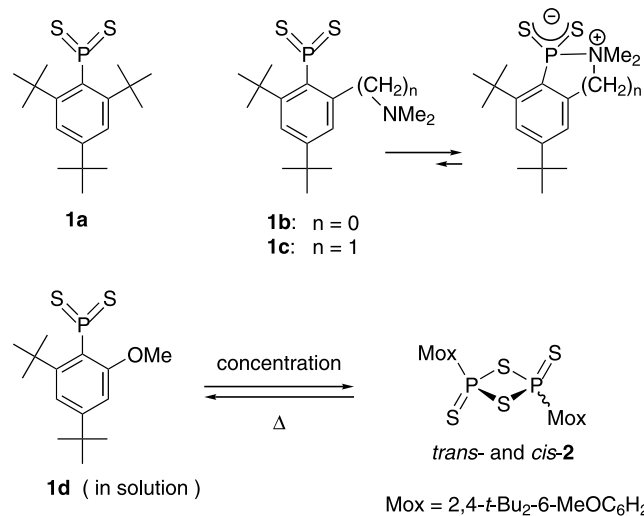
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**Abstract**—Fluorenylidene phosphines having a 2,4-di-*t*-butyl-6-methoxyphenyl, 2,4-di-*t*-butyl-6-(methoxymethyl)phenyl or 2,4-di-*t*-butyl-6-(phenoxyethyl)phenyl group were prepared.  $^{31}\text{P}$  NMR chemical shifts of the fluorenylidene phosphines indicated that electron-donating effects through space are not so strong between the alkoxy group and the double-bonded phosphorus atom. The structure of a tungsten carbonyl complex of [2,4-di-*t*-butyl-6-(phenoxyethyl)phenyl](fluorenylidene)phosphine was analyzed by X-ray crystallography. © 2002 Elsevier Science Ltd. All rights reserved.

Studies on intramolecular donor-stabilized species<sup>1</sup> have recently been developed in main-group element chemistry. Tuning of the electronic effect in such systems and comparison of properties of the electronically perturbed compounds with those of kinetically stabilized compounds are now subjects of interest. We have studied the kinetic stabilization in multiple-bonded phosphorus compounds. The 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to Mes\*) group is a typical and powerful bulky protecting group, and by utilizing this substituent we and others have successfully prepared various types of phosphorus compounds of unusual structures<sup>2</sup> such as diphosphenes,<sup>3</sup> phosphacumulenes,<sup>4</sup> phospharadialenes,<sup>5</sup> and dichalcogenoxophosphoranes.<sup>6</sup> In the course of our continuing efforts towards systematic modification of the Mes\* group, we have examined various substituents such as 2,4-di-*t*-butyl-6-(dialkylamino)phenyl,<sup>7</sup> 2,4-di-*t*-butyl-6-(dialkylaminomethyl)phenyl,<sup>8</sup> 2,4-di-*t*-butyl-6-methoxyphenyl,<sup>9</sup> and 2,4-di-*t*-butyl-6-(methoxymethyl)phenyl.<sup>10</sup> For example, we have prepared dithioxophosphorane derivatives **1a–f** (Schemes 1 and 2). The Mes\*-substituted dithioxophosphorane **1a** is thermally stable under an inert atmosphere,<sup>6a–c</sup> whereas donor-stabilized compounds **1b**<sup>7a</sup> and **1c**<sup>8a</sup> are stable even in air. On the other hand, compound **1d** is stable only in a solution and dimerizes

to *trans*- and *cis*-2 upon concentration.<sup>9</sup> Compound **1e** rearranged to **3**<sup>10b</sup> at 180°C.<sup>11</sup> A similar rearrangement proceeds in the case of **1f** to give **4**.<sup>12</sup>

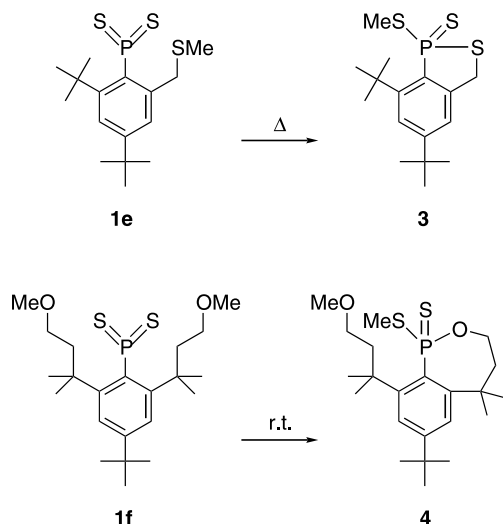
The research of structure–property relationships of other essentially reactive species, such as phosphathenes (phosphaalkenes), is also important. Polarization of the  $\text{P}=\text{C}$  bond in phosphathenes (in the classical notation,  $\text{P}^{\delta+}=\text{C}^{\delta-}$ ) is supposed to be not so large as that of the  $\text{P}=\text{S}$  bond ( $\text{P}^{\delta+}=\text{S}^{\delta-}$ ) in dithioxophosphoranes. Thus, it is interesting to know how the donor-stabilization operates in the two different sys-



Scheme 1.

**Keywords:** phosphorus compounds; phosphathenes; donors; steric effects.

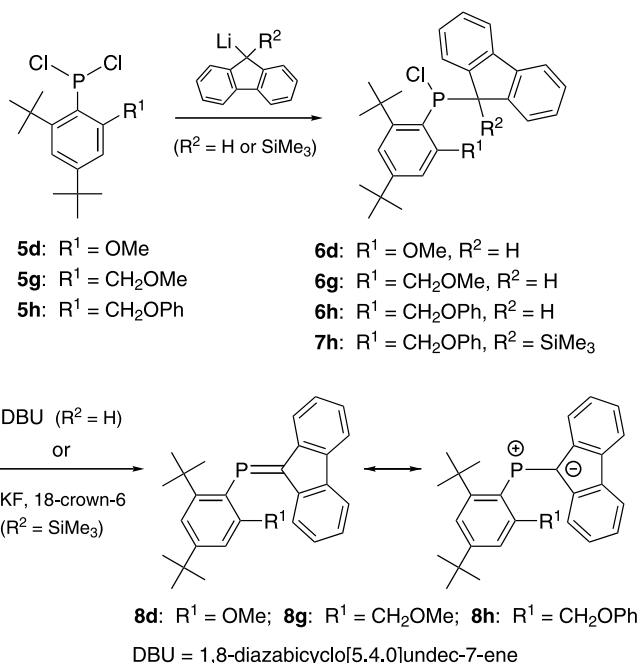
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Scheme 2.

tems. We now report here the preparation and properties of phosphathenes bearing bulky aryl substituents with electron-donating alkoxy or aryloxy groups at the *o*-position.<sup>13</sup>

First, a fluorenylidene phosphine bearing a 2,4-di-*t*-butyl-6-methoxyphenyl (abbreviated to Mox) group was prepared as follows (Scheme 3): 9-fluorenyllithium was allowed to react with dichlorophosphine **5d**<sup>9a</sup> in THF at  $-78^{\circ}\text{C}$  to form chloro(fluorenyl)phosphine **6d** [ $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ )  $\delta=83.9$ ; MS  $m/z$  (rel. intensity) 452 ( $\text{M}^++2$ ; 13), 450 ( $\text{M}^+$ ; 34), and 285 ( $\text{Mox-PCl}^+$ ; 100)]. Then **6d** in THF was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of molecular sieves 4 Å MS to give fluorenylidene phosphine **8d** in 70% yield.<sup>14</sup>



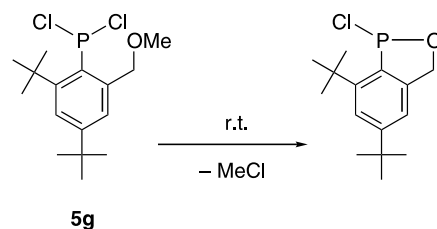
Scheme 3.

Then preparation of **8g**, bearing the 2,4-di-*t*-butyl-6-(methoxymethyl)phenyl, was examined in a similar manner. Although the formation of a trace amount of **8g** was observed by  $^{31}\text{P}$  NMR spectroscopy after the successive treatment of dichlorophosphine **5g** with 9-fluorenyllithium and DBU, an attempted isolation of **8g** failed due to decomposition. Moreover, the instability of dichlorophosphine **5g** seems to limit its synthetic applications: As we have observed previously,<sup>10</sup> a cyclization reaction of **5g** occurs<sup>15</sup> at room temperature (Scheme 4) to eliminate chloromethane.

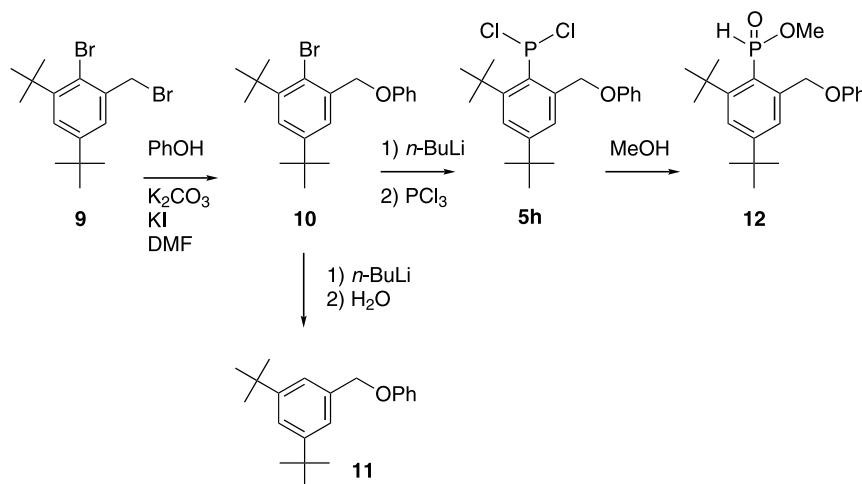
Thus, in order to suppress the instability, phenoxymethyl congener **5h** (as an alternative starting material for various phosphorus species) was prepared as follows (Scheme 5): a mixture of 2-bromo-1-bromo-methyl-3,5-di-*t*-butylbenzene (**9**,<sup>10a</sup> 5.00 g, 13.8 mmol), phenol (16.3 mmol), potassium carbonate (22.7 mmol), and potassium iodide (1.5 mmol) in DMF (30 mL) was stirred at room temperature for 28 h to give **10** in 88% yield.

When bromobenzene **10** was treated with butyllithium and water successively, compound **11** was formed to show that the halogen–metal exchange reaction proceeded. Reaction of **10** with butyllithium followed by treatment with  $\text{PCl}_3$  afforded dichlorophosphine **5h** [ $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta=162.3$ ; MS  $m/z$  (rel. intensity) 400 ( $\text{M}^++4$ ; 0.3), 398 ( $\text{M}^++2$ ; 1), 396 ( $\text{M}^+$ ; 2), and 303 ( $\text{M}^+-\text{OPh}$ ; 100)]. Dichlorophosphine **5h** is stable at room temperature under an inert atmosphere and the cyclization reaction did not occur, while **5h** reacted with methanol to give **12**, in contrast to **5g**.

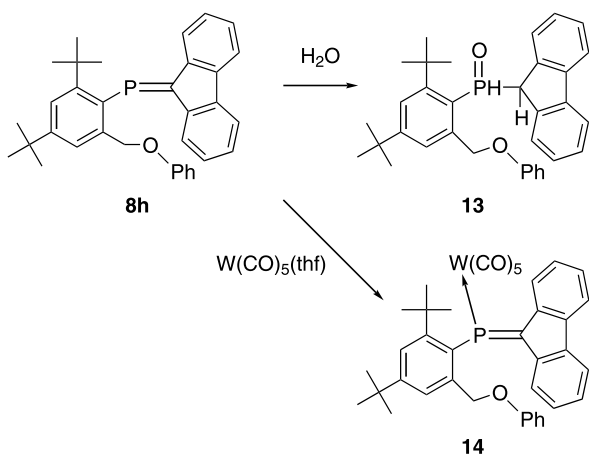
Reaction of **5h** with 9-fluorenyllithium gave chloro(fluorenyl)phosphine **6h** [ $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta=82.2$ ; MS  $m/z$  (rel. intensity) 528 ( $\text{M}^++2$ ; 0.8), 526 ( $\text{M}^+$ ; 2), and 165 ( $\text{C}_{13}\text{H}_9^+$ ; 100)] (Scheme 3). Treatment of **6h** with DBU formed the corresponding fluorenylidene phosphine **8h**, although an attempted isolation of **8h** from the reaction mixture failed because a decomposition reaction occurred during the isolation process. However, **8h** was successfully isolated in the reaction of **7h** [ $^{31}\text{P}$  NMR (162 MHz,  $\text{THF}-\text{C}_6\text{D}_6$ )  $\delta=95.8$ ] with potassium fluoride in the presence of 18-crown-6 (83% yield based on **10**). Although fluorenylidene phosphine **8h** itself was not so stable in air and was gradually hydrolyzed by moisture to give **13** (Scheme 6), pentacarbonyltungsten complex **14** [formed by reaction of **8h** with  $\text{W}(\text{CO})_5(\text{thf})$  in THF, 22% yield] was stable in air.



Scheme 4.



Scheme 5.



Scheme 6.

The structure of complex **14** was analyzed by X-ray crystallography.<sup>19</sup> Fig. 1 shows an ORTEP<sup>20</sup> drawing of the molecular structure. The atoms W(1), P(1), C(1), C(2), and C(13) lie on the same plane within  $\pm 0.09$  Å, and the atom C(14) deviates 0.37(1) Å from the plane. Sums of the angles around P(1) and C(1) are 358.2 and 359.8°, respectively, indicating that the pyramidalization at the phosphorus center is small and the phosphorus–carbon double bond system is essentially planar in **14**. The aromatic ring C(15)–C(19) is nearly perpendicular to the  $-\text{P}=\text{C}<$  plane (interplanar angle: 91.5(2)°). The bond length of the phosphorus–carbon double bond in **14** is 1.692(8) Å, which is longer than that in 1,6-diphosphahexa-1,5-diene complex **15** [1.66(7) Å]<sup>21</sup> or 1-phosphabutatriene complex **16** [1.664(6) Å]<sup>22</sup> (Chart 1). This fact may suggest that the bond order of the  $\text{P}=\text{C}$  bond in **14** is decreased by a slight interaction with the phenoxy group, although the phosphorus–tungsten bond length in **14** [2.496(2) Å] is shorter than that for **15** [2.539(2) Å] and close to that for **16** [2.506(1) Å].

The distance between the phosphorus atom and the oxygen atom of the phenoxy group might indicate the

importance of intramolecular coordination. The value for **14** is 3.438(6) Å, which means it is slightly out of van der Waals contact [the sum of van der Waals radii of the atoms is 3.30 Å],<sup>23</sup> in contrast to the case of **1c** or the donor-stabilized silene **17**, where the nitrogen atoms participate in the intramolecular donor stabilization. The distance between the phosphorus center and the nitrogen atom is 1.921(8) Å in **1c** [sum of van der Waals radii of the atoms (3.44 Å)].<sup>8a,23</sup> In **17**, the distance between the nitrogen atom and the silicon atom is 2.004(2) Å, which is much shorter than the sum of van der Waals radii of the atoms (3.54 Å).<sup>13b,23</sup>

Table 1 shows <sup>31</sup>P NMR data of fluorenylidene phosphines **8d,g,h**, and some of the related phosphathenes. A signal of **8d** showed a higher-field shift in <sup>31</sup>P NMR spectrum, compared to that of the kinetically stabilized molecule **8a**,<sup>16</sup> while a chemical shift of **8d** was very close to those of methoxymethyl congener **8g** and phenoxy methyl congener **8h**. Although the anisotropic effect of the aromatic ring in **8h** should be taken into account, these facts may indicate that the alkoxy group has an electron-donating effect on the phosphorus atom in **8d,g,h**. However, the electron-donating effect in **8d,g,h** is not so strong according to the <sup>31</sup>P NMR study. This resembles the case of **1d**: <sup>31</sup>P NMR signal of **1d** [ $\delta_{\text{P}}(\text{C}_6\text{D}_6) = 277.6$ ] is close to that of **1a** [ $\delta_{\text{P}}(\text{CDCl}_3) =$

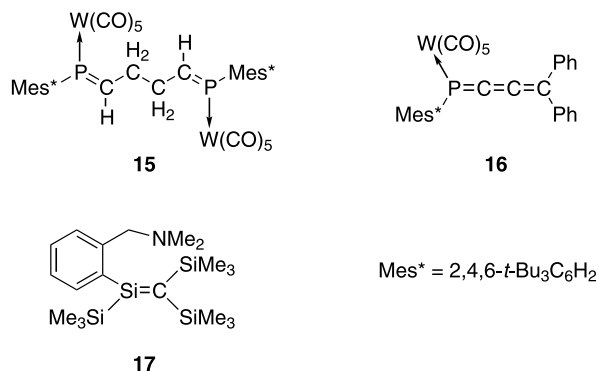
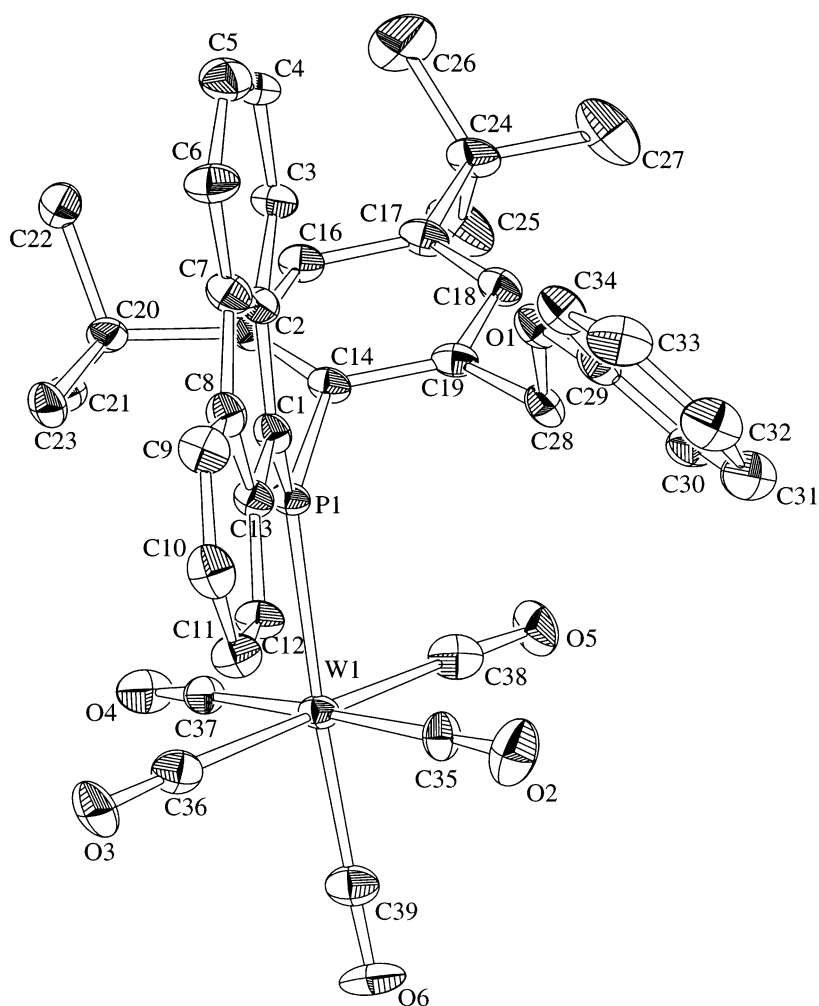


Chart 1.



**Figure 1.** Molecular structure of **14**, showing the atomic labeling scheme with thermal ellipsoids (30% probability). Some selected bond lengths (Å) and angles (°): P(1)–W(1), 2.496(2); P(1)–C(1), 1.692(8); P(1)–C(14), 1.834(7); W(1)–P(1)–C(1), 133.3(3); W(1)–P(1)–C(14), 115.3(3); P(1)–C(1)–C(2), 129.6(6); P(1)–C(1)–C(13), 125.2(6); C(1)–P(1)–C(14), 109.6(4); C(2)–C(1)–C(13), 105.0(6).

298.2] and the oxygen–phosphorus interaction in **1d** seems to be weak, while the chemical shift of **1c** [ $\delta_{\text{P}}(\text{CDCl}_3) = 149.6$ ] appears upfield by ca. 150 ppm to that of **1a** and strong nitrogen–phosphorus interaction was observed in the crystal of **1c** (see above). In addition, the instability of **8d,g,h** suggests that the donor groups in these molecules do not sufficiently stabilize the phosphorus–carbon double bond, while kinetically stabilized **8a** is very stable at room temperature even in air.

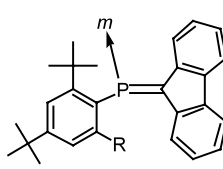
In summary, an alkoxy group or alkoxymethyl group at the *o*-position in arylphosphaethene does not strongly stabilize the P=C system, similarly to the cases of dithioxophosphorane derivatives **1d,f**. Nevertheless, modification of the 2,4-di-*t*-butyl-6-(phenoxymethyl)-phenyl group in the phenyl moiety seems to be promising for the purpose of fine-tuning the electronic state of a multiple-bonded phosphorus compound, because the electron-donating ability of the oxygen atom can be changed by introducing various functional groups into

the aromatic ring. Further studies on structure–property relationships of the phosphoethenes are in progress.

#### Selected data of compounds

**8d**: Yellow powder, mp 142–145°C;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta = 1.40$  (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);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta = 171.8$  (d,  $^1J_{\text{PC}} = 40.1$  Hz, P=C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{C}_6\text{D}_6$ )  $\delta = 246.4$ ; UV (hexanes) 225 (log  $\epsilon$  4.2), 238 (4.6), 253 (4.3), 266 (4.4) 270 (4.4), 275 (4.5), 308 (3.6), and 363 nm (4.2); IR (KBr) 1647, 1589, 1442, 1394, 1325, 1207, 1055, 847, 769, and 729  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (rel intensity) 414 ( $\text{M}^+$ ; 100), 249 ( $\text{MoxP}^+ - 1$ ; 75), 233 ( $\text{MoxP}^+ - \text{Me} - 2$ ; 6), 219 ( $\text{Mox}^+$ ; 5), 193 ( $\text{M}^+ - \text{Mox} - 2$ ; 20), 165 (Fluorene $^+$ ; 42), and 57 (*t*-Bu $^+$ ; 20). Found:  $m/z$  414.2115. Calcd for  $\text{C}_{28}\text{H}_{31}\text{OP}$ : M, 414.2113.

**Table 1.**  $^{31}\text{P}$  NMR data of fluorenylidene phosphines in  $\text{CDCl}_3$ 

R	<i>m</i>		$\delta_{\text{P}}^{\text{a}}$	$J_{\text{WP}}$ (Hz)	
	<i>t</i> -Bu	None	( <b>8a</b> )	256.5 <sup>b</sup>	
	<i>i</i> -Pr <sup>c</sup>	None		257.2	
	Me <sup>c</sup>	None		254.0	
	OMe	None	( <b>8d</b> )	247.9	
	CH <sub>2</sub> OMe	None	( <b>8g</b> )	249.7	
	CH <sub>2</sub> OPh	None	( <b>8h</b> )	245.8	
	CH <sub>2</sub> OPh	W(CO) <sub>5</sub>	( <b>14</b> )	193.9	281.4

<sup>a</sup> Relative to external 85%  $\text{H}_3\text{PO}_4$ .

<sup>b</sup> In Ref. 16,  $\delta_{\text{P}}=253.1$  in  $\text{C}_6\text{H}_6$ .

<sup>c</sup> Formed from the corresponding dichlorophosphines<sup>17,18</sup> by a method similar to that for **8d**. Attempted isolation using silica gel column chromatography failed.

**8h:** Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta=1.44$  (9H, s, *p*-*t*-Bu), 1.54 (9H, s, *o*-*t*-Bu), 4.82 (1H, d,  $^2J_{\text{HH}}=12.7$  Hz,  $\text{CHH}'\text{O}$ ), 5.30 (1H, d,  $^2J_{\text{HH}}=12.7$  Hz,  $\text{CHH}'\text{O}$ ), 6.10 (1H, dd,  $J=8.0$  Hz and  $J=2.6$  Hz), 6.8–6.9 (4H, m), 7.16 (2H, m), 7.25 (2H, d,  $J=7.5$  Hz), 7.35 (2H, dd  $J=7.5$  Hz and  $J=7.5$  Hz), 7.56 (1H, d,  $J=1.6$  Hz), 7.63 (2H, dd,  $J=8.0$  Hz and  $J=8.0$  Hz), 7.68 (1H, br. s), and 8.14 (1H, dd,  $J=8.0$  Hz and  $J=7.5$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta=70.5$  (d,  $^3J_{\text{PC}}=9.1$  Hz,  $\text{CH}_2\text{O}$ ), 173.4 (d,  $^1J_{\text{PC}}=43.1$  Hz,  $\text{P}=\text{C}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta=245.8$ ; UV (hexanes) 256 (log  $\epsilon$  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  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (rel. intensity) 490 ( $\text{M}^+$ ; 65), 397 ( $\text{M}^+-\text{OPh}$ ; 100), 383 ( $\text{M}^+-\text{CH}_2\text{OPh}$ ; 34), 341 ( $\text{M}^+-\text{OPh}-t\text{-Bu}+1$ ; 41), 165 ( $\text{C}_{13}\text{H}_9^+$ ; 32), 149 (84), and 57 (*t*-Bu<sup>+</sup>; 86). Found:  $m/z$  490.2432. Calcd for  $\text{C}_{34}\text{H}_{35}\text{OP}$ : M, 490.2426.

**10:** Colorless powder, mp 62–64°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta=1.36$  (9H, s, *p*-*t*-Bu), 1.63 (9H, s, *o*-*t*-Bu), 5.22 (2H, s,  $\text{CH}_2\text{O}$ ), 7.05 (2H, d,  $J=7.5$  Hz), 7.10 (1H, t,  $J=8.7$  Hz), 7.38 (2H, dd,  $J=8.7$  Hz and  $J=7.5$  Hz), 7.53 (1H, d,  $J=2.4$  Hz), and 7.55 (1H, d,  $J=2.4$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta=71.6$  ( $\text{CH}_2\text{O}$ ); IR (KBr) 1595, 1495, 1471, 1427, 1387, 1365, 1265, 1174, 1080, 1020, 885, 835, 750, and 692  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (rel. intensity) 376 ( $\text{M}^{+2}$ ; 10), 374 ( $\text{M}^+$ ; 10), 283 ( $\text{M}^+-\text{OPh}+2$ ; 75), 281 ( $\text{M}^+-\text{OPh}$ ; 76), 187 ( $\text{M}^+-\text{Br}-\text{CH}_2\text{OPh}+1$ ; 6), and 57 (*t*-Bu<sup>+</sup>; 100). Found:  $m/z$  374.1247. Calcd for  $\text{C}_{21}\text{H}_{27}\text{BrO}$ : M, 374.1245.

**11:** Colorless crystals, mp 53–54°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta=1.36$  (18H, s, *t*-Bu), 5.05 (2H, s,  $\text{CH}_2\text{O}$ ), 6.99 (1H, t,  $J=7.6$  Hz), 7.04 (2H, dd,  $J=8.8$  Hz and  $J=1.2$  Hz), 7.30–7.35 (4H, m), and 7.43 (1H, t,  $J=1.8$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta=71.2$  ( $\text{CH}_2\text{O}$ ); IR (KBr) 1599, 1494, 1473, 1367, 1295, 1238, 1172, 1081, 1014, 879, 829, 752, 713, and 692  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (rel. intensity) 297 ( $\text{M}^{+1}$ ; 100). Found:  $m/z$  296.2132. Calcd for  $\text{C}_{21}\text{H}_{28}\text{O}$ : M, 296.2140.

**12:** Colorless crystals, mp 77–79°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta=1.31$  (9H, s, *p*-*t*-Bu), 1.57 (9H, s,

*o*-*t*-Bu), 3.84 (3H, d,  $^3J_{\text{PH}}=12.3$  Hz, OMe), 5.51 (1H, d,  $^2J_{\text{HH}}=13.0$  Hz,  $\text{CHH}'\text{O}$ ), 5.61 (1H, d,  $^2J_{\text{HH}}=13.0$  Hz,  $\text{CHH}'\text{O}$ ), 6.97 (1H, t,  $J=7.5$  Hz), 7.05 (2H, d,  $J=8.6$  Hz), 7.30 (2H, dd,  $J=8.6$  Hz and  $J=7.5$  Hz), 7.51 (1H, d,  $J=6.0$  Hz), 7.64 (1H, s), and 8.46 (1H, d,  $^1J_{\text{PH}}=569.4$  Hz, PH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta=53.8$  (d,  $^2J_{\text{PC}}=6.1$  Hz, P-OMe) and 68.5 (d,  $^3J_{\text{PC}}=6.4$  Hz,  $\text{CH}_2\text{O}$ );  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta=31.9$  (d,  $^1J_{\text{PH}}=569.6$  Hz); IR (NaCl) 3060–2870 (br.), 2431, 1727, 1600, 1546, 1496, 1402, 1375, 1240, 1220, 1010, 883, 838, 790, 855, and 692  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (rel. intensity) 374 ( $\text{M}^+$ ; 8), 356 ( $\text{M}^+-\text{O}-\text{H}-1$ ; 11), and 281 ( $\text{M}^+-\text{OPh}$ ; 100). Found:  $m/z$  374.2008. Calcd for  $\text{C}_{22}\text{H}_{31}\text{O}_3\text{P}$ : M, 374.2011.

**13:** Colorless powder, mp 206–208°C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta=1.03$  (9H, s, *p*-*t*-Bu), 1.43 (9H, s, *o*-*t*-Bu), 4.95 (1H, dd,  $^2J_{\text{PH}}=24.5$  Hz,  $^3J_{\text{HH}}=7.0$  Hz, P-CH), 5.35 (1H, d,  $^2J_{\text{HH}}=11.3$  Hz,  $\text{CHH}'\text{O}$ ), 6.25 (1H, d,  $J=7.5$  Hz), 6.41 (1H, d,  $^2J_{\text{HH}}=11.3$  Hz,  $\text{CHH}'\text{O}$ ), 6.91 (1H, dd,  $J=7.5$  Hz and  $J=7.5$  Hz), 6.98 (1H, t,  $J=7.3$  Hz), 7.08 (1H, dd,  $^1J_{\text{PH}}=502.6$  Hz and  $^3J_{\text{HH}}=7.0$  Hz, PH), 7.10 (2H, d,  $J=8.0$  Hz), 7.26–7.31 (1H, m), 7.30 (2H, dd,  $J=8.0$  Hz and  $J=7.3$  Hz), 7.40 (1H, dd,  $J=7.5$  Hz and  $J=7.5$  Hz), 7.47 (1H, dd,  $J=7.5$  Hz and  $J=7.5$  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);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta=50.8$  (d,  $^1J_{\text{PC}}=56.3$  Hz, P-CH) and 68.5 (d,  $^3J_{\text{PC}}=6.0$  Hz,  $\text{CH}_2\text{O}$ );  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta=30.8$  (dd,  $^1J_{\text{PH}}=502.6$  Hz and  $^2J_{\text{PH}}=24.5$  Hz); IR (KBr) 3133, 2998, 1596, 1485, 1448, 1230, 1180, 1008, 800, and 748  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (rel. intensity) 508 ( $\text{M}^+$ ; 10), 415 ( $\text{M}^+-\text{OPh}$ ; 13), 343 ( $\text{M}^+-\text{C}_{13}\text{H}_9$ ; 51), 325 ( $\text{M}^+-\text{C}_{13}\text{H}_{10}-\text{OH}$ ; 11), 249 ( $\text{M}^+-\text{C}_{13}\text{H}_{10}-\text{OPh}$ ; 42), and 165 ( $\text{C}_{13}\text{H}_9^+$ ; 100). Found:  $m/z$  508.2502. Calcd for  $\text{C}_{34}\text{H}_{37}\text{O}_2\text{P}$ : M, 508.2531.

**14:** Orange prisms, mp 167°C (decomp.);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta=1.43$  (9H, s, *p*-*t*-Bu), 1.57 (9H, s, *o*-*t*-Bu), 5.17 (1H, dd,  $^2J_{\text{HH}}=12.3$  Hz and  $^4J_{\text{PH}}=1.6$  Hz,  $\text{CHH}'\text{O}$ ), 5.52 (1H, dd,  $^2J_{\text{HH}}=12.3$  Hz and  $^4J_{\text{PH}}=2.2$  Hz,  $\text{CHH}'\text{O}$ ), 6.44 (1H, dd,  $J=8.0$  Hz and  $J=3.6$  Hz), 6.64–6.66 (2H, m), 6.83–6.90 (2H, m), 7.08–7.11 (2H, m), 7.24 (1H, ddd,  $J=7.4$  Hz,  $J=7.4$  Hz, and

$J=2.4$  Hz), 7.34 (1H, dd,  $J=7.8$  Hz and  $J=7.8$  Hz), 7.41 (1H, ddd,  $J=7.4$  Hz,  $J=7.4$  Hz, and  $J=2.0$  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,  $J=7.6$  Hz and  $J=4.0$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta=69.7$  (d,  $^3J_{\text{PC}}=8.6$  Hz,  $\text{CH}_2\text{O}$ ), 168.2 (d,  $^1J_{\text{PC}}=40.4$  Hz,  $\text{P}=\text{C}$ ), 195.9 (d,  $^2J_{\text{PC}}=9.6$  Hz, satellite  $^1J_{\text{WC}}=125.7$  Hz,  $\text{CO}_{\text{eq}}$ ), and 198.8 (d,  $^2J_{\text{PC}}=31.7$  Hz,  $\text{CO}_{\text{ax}}$ );  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta=193.9$  (satellite,  $^1J_{\text{WP}}=281.4$  Hz); UV (hexanes) 211 (log  $\epsilon$  4.90), 337 (3.88), and 474 nm (4.38); IR (KBr) 2071, 1957, 1919, 1597, and 1232  $\text{cm}^{-1}$ ; MS (70 eV)  $m/z$  (rel. intensity) 814 ( $\text{M}^+$ ; 6), 730 ( $\text{M}^+-3\text{CO}$ ; 8), 674 ( $\text{M}^+-5\text{CO}$ ; 8), 490 ( $\text{M}^+-\text{W}(\text{CO})_5$ ; 42), 397 ( $\text{M}^+-\text{OPh}-\text{W}(\text{CO})_5$ ; 63), 341 ( $\text{M}^+-t\text{-Bu}-\text{OPh}-\text{W}(\text{CO})_5$ ; 23), 165 ( $\text{Flu}^++1$ ; 34), 57 ( $t\text{-Bu}^+$ ; 89), and 28 ( $\text{CO}^+$ ; 100).

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Hydrogen atoms were included but not refined.  $R_1=0.059$ ,  $R=0.116$ ,  $R_w=0.151$ . Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-190819).

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