Utilization of 2,4-Di-*t*-butyl-6-(methoxymethyl)phenyl as a New Sterically Protecting Group[1)]

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A sterically hindered bromobenzene, 2-bromo-1,5-di-*t*-butyl-3-(methoxymethyl)benzene, was prepared and converted to the corresponding phosphonous dichloride. The dichloride was then utilized to stabilize a low-coordinate phosphorus compound such as 1-[2,4-di-*t*-butyl-6-(methoxymethyl)phenyl]-2-(2,4,6-tri-*t*-butylphenyl)diphosphene. Furthermore, the dichloride gave a cyclization product 1-chloro-2,1-oxaphosphaindan with elimination of chloromethane on standing at room temperature.

Compounds with low coordinated heavier main group elements such as phosphorus can be kinetically stabilized by bulky substituents (steric protection).[2)] 2,4,6-Tri-*t*-butylphenyl group (hereafter abbreviated to Ar) is one of the typical and powerful bulky protecting groups[3)] and by utilizing this substituent we and others have successfully prepared various types of low coordinated tervalent phosphorus compounds such as diphosphenes, phosphaalkenes, phosphacumulenes, and phosphaalkynes.[2)] Moreover, we have examined 2,4-di-*t*-butyl-6-methylphenyl,[4)] 2,6-di-*t*-butylphenyl,[5)] and 2,4,6-tri-*t*-pentylphenyl[6)] groups as protecting auxiliary to evaluate the stabilization effect of substituents at the ortho positions of the aromatic protecting groups. We are now engaged in developing new protecting groups which are expected to contribute both kinetic and thermodynamic stabilization.

Very recently, we have reported the utilization of 2,4-di-*t*-butyl-6-(dimethylamino)phenyl group (abbreviated to Mx; Mx stands for octamethylxylidine derivative) as a new protecting group,[7)] where one of the *o*-*t*-butyl groups in the Ar is replaced by an electron-donating dimethylamino group. Utilizing this substituent, we have prepared MxP=Se for the first time[7)] as well as $MxPS_2$ and $MxPSe_2$ as stable compounds. Since then, we have been interested in the role of the nitrogen lone pair of the Mx group and we are modifying the Mx group with respect to the kind of element as well as the position of the hetero atom. Here, we report the utilization of 2,4-di-*t*-butyl-6-(methoxymethyl)phenyl group (abbreviated to Momx; Momx stands for (methoxymethyl-*m*-xylene derivative) as a novel protecting group carrying oxygen at the δ-position to the phosphorus atom (Chart 1).

Results and Discussion

2-Bromo-1,5-di-*t*-butyl-3-methylbenzene[8)] was brominated by *N*-bromosuccinimide (NBS) to give 2-bromo-1-(bromomethyl)-3,5-di-*t*-butylbenzene (**1**) in 77% yield together with 2-bromo-1,5-di-*t*-butyl-3-(dibromomethyl)benzene (**2**) in 1% yield. The reaction of **1** with sodium methoxide afforded 2-bromo-1,5-di-*t*-butyl-3-(methoxymethyl)benzene (**3**) in 85% yield. Lithiation of **3** with butyllithium followed by the reaction with phosphorus trichloride at −78 °C gave the corresponding phosphonous dichloride **4a** [δ_p ($CDCl_3$) 162.8]. The structure of **4a** was confirmed by a quenching experiment with methanol in the presence of triethylamine; the reaction gave dimethyl 2,4-di-*t*-butyl-6-(methoxymethyl)phenylphosphonite (**5a**; 15% yield) and methyl 2,4-di-*t*-butyl-6-(methoxymethyl)phenylphosphinate (**6a**; 34%) after treatment with column chromatography (SiO_2/CH_2Cl_2), together with 1,3-di-*t*-butyl-5-(methoxymethyl)benzene (**7**; 26% yield). The formation of **6a** is considered to be due to the hydrolysis reaction during the chromatographic process, because the ^{31}P NMR spectrum of the reaction mixture before chromatography indicated almost quantitative formation of **5a**. Compound **7** seems to have been formed from **5a** and/or **6a** during the column chromatographic procedure. It should be noted that the phosphonous dichloride **4a** gradually decomposed to 2,1-oxaphosphaindan **8** and chloromethane in THF at room temperature. Compound **8** was further hydrolyzed by aerial moisture to give the corresponding oxaphosphaindan oxide **9**. The yield of **9** was 32% based on **3** after chromatography. Thus, **4a** was used immediately after preparation below 0 °C without isolation process (Scheme 1).

Finally, 1-[2,4-di-*t*-butyl-6-(methoxymethyl)phenyl]-2-(2,4,6-tri-*t*-butylphenyl)diphosphene (**10a**) was obtained by the reaction of **4a** with lithium 2,4,6-tri-*t*-butylphenylphosphide followed by the dehydrochlorination reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The Momx group is bulky enough to permit isolation of the diphosphene **10a**. The stability of **10a**, however, is not so high as 1-[2,4-di-*t*-butyl-6-methylphenyl]-2-(2,4,6-tri-*t*-butylphenyl)diphosphene (**10b**)[4)] and actually **10a** decomposed partially on standing at room temperature. Table 1 shows the ^{31}P NMR data of **10a** and some related diphosphenes. Both chemical shifts (δ_p) and spin-coupling constants ($^1J_{pp}$) of **10a** are very similar to those of **10b**, respec-

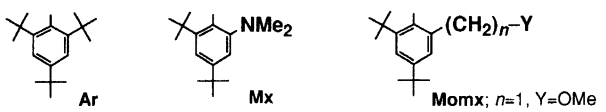
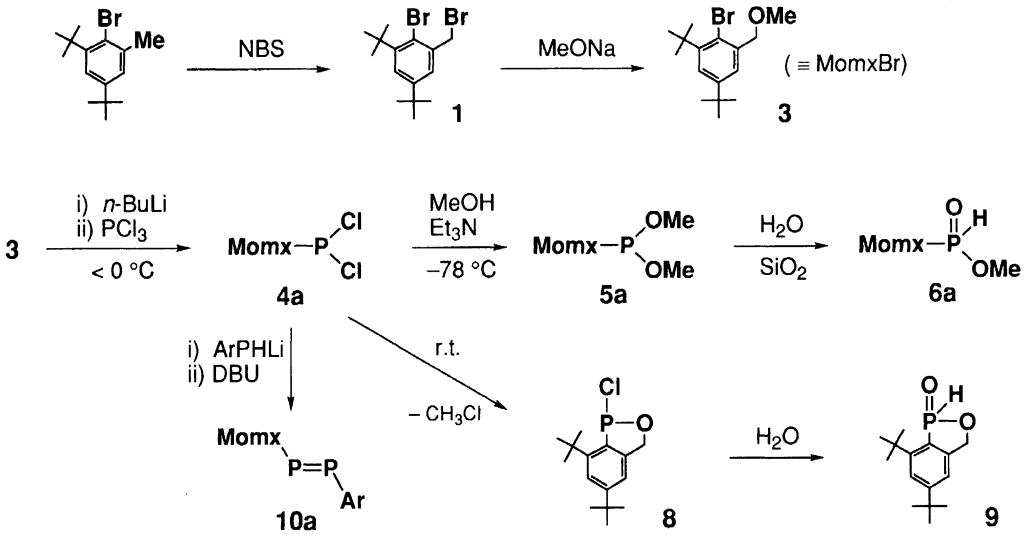


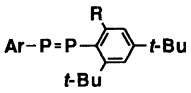
Chart 1.



Momx = 2,4-*t*-Bu_2-6-($MeOCH_2$)C_6H_2; Ar = 2,4,6-*t*-$Bu_3C_6H_2$; NBS = *N*-bromosuccinimide; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Scheme 1.

Table 1. ^{31}P NMR Data of Diphosphenes **10a—d**

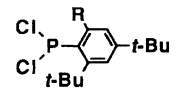
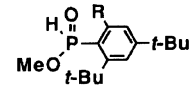
Compound[a]	R	δ_P in C_6D_6	$^1J_{PP}$/Hz
	**10a**: CH_2OMe	473.9 and 517.9	583.9
	10b: Me[b]	480.1 and 517.0	583.5
	10c: *t*-Bu[c]	492.4	—
	10d: NMe_2[d]	461.0 and 475.4	562.9

a) Ar=2,4,6-*t*-$Bu_3C_6H_2$. b) Data taken from Ref. 4. c) Data taken from Ref. 3. d) Data taken from Ref. 9.

tively, though the diphosphene **10d** bearing the Mx-group appears at the higher field with a smaller coupling constant. Similarly, the chemical shifts and spin-coupling constants of **4a** and **6a** are very close to those of **4b** and **6b**, respectively, compared with those of **4d** and **6d** (Table 2).

These facts may indicate that the oxygen atom in **10a** does not strongly affect the phosphorus–phosphorus double bond at least on the ^{31}P NMR time scale. However, a transient interaction between oxygen and phosphorus in **4a** may become important to cause cyclization to **8**. Thus the Momx group is a new sterically protecting group having potentially through-space interaction.

Table 2. ^{31}P NMR Data of Dichlorophosphines **4a—d** and Methyl Phosphinates **6a—d**

Compound	R	δ_P in $CDCl_3$	$^1J_{PH}$/Hz
	**4a**: CH_2OMe	162.8	—
	4b: Me[a]	167.5	—
	4c: *t*-Bu[b]	153.8	—
	4d: NMe_2[c]	154.2	—
	**6a**: CH_2OMe	31.5	562.6
	6b: Me[d]	32.1	563.0
	6c: *t*-Bu[e]	30.3	566.2
	6d: NMe_2[f]	29.2	591.1

a) Data taken from Ref. 4. b) Ref. 3, see Note 11. c) Ref. 7, see Note 11. d) Ref. 4, but no NMR data were reported for **6b**. e) Ref. 10, see Note 11. f) Ref. 7.

Experimental

Instruments. Melting points were taken on a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^{1}H NMR (200 MHz) spectra, ^{13}C NMR (50 MHz) spectra, and ^{31}P NMR (81 MHz) spectra were recorded on a Bruker AC-200P 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. MS (70 eV) spectra were taken on either JEOL HX-110 or Hitachi M-2500S spectrometer.

2-Bromo-1-(bromomethyl)-3,5-di-*t*-butylbenzene (1). A mixture of 2-bromo-1,5-di-*t*-butyl-3-methylbenzene (119.76 g, 0.423 mol)[8] and NBS (75.34 g, 0.423 mol) in carbon tetrachloride (180 ml) was refluxed for 3.5 h. Insoluble material was filtered off and the filtrate was distilled under reduced pressure to afford 117.19 g of **1** (bp 150—155 °C, 2.0 mmHg, 1 mmHg=133.322 Pa). In addition, column chromatographic separation (SiO_2/hexane) of the residue gave 1.54 g of **1**, 2.36 g (1%) of 2-bromo-1,5-di-*t*-butyl-3-(dibromomethyl)benzene (**2**), and 15.66 g (13% recovery) of the starting bromobenzene. The combined yield of **1** was thus 118.73 g (77%).

1: Colorless scales; mp 52—54 °C(EtOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.32 (9H, s, Bu^t), 1.56 (9H, s, Bu^t), 4.72 (2H, s, CH_2Br), 7.34 (1H, d, ^4J=2.5 Hz, arom.), and 7.46 (1H, d, ^4J=2.5 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$)

δ=30.8 ($C\underline{Me}_3$), 31.2 ($C\underline{Me}_3$), 34.7 ($\underline{C}Me_3$), 36.8 (CH_2), 37.5 ($\underline{C}Me_3$), 122.1 (arom.), 125.9 (arom.-CH), 126.5 (arom.-CH), 138.1 (arom.), 148.4 (arom.), and 150.0 (arom.); UV (hexane) 238 (sh, log ε 4.0), 278 (sh, 2.9), and 288 nm (sh, 2.8); IR (KBr) 1394, 1363, 1213, 1018, 883, 736, and 590 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 360 (M^+; 13), 345 (M^+-Me; 10), 281 (M^+-Br; 100), and 57 (t-Bu^+; 10). Found: *m/z* 360.0127. Calcd for $C_{15}H_{22}Br_2$: M, 360.0088. Found: C, 49.63; H, 5.98%. Calcd for $C_{15}H_{22}Br_2$: C, 49.75; H, 6.12%.

2: Colorless crystals; mp 102.5—104 °C (hexane); ^1H NMR δ=1.36 (9H, s, Bu^t), 1.55 (9H, s, Bu^t), 7.41 (1H, s, $CHBr_2$), 7.46 (1H, d, ^4J=2.4 Hz, arom.), and 7.98 (1H, d, ^4J=2.4 Hz, arom.); $^{13}C\{^1H\}$ NMR δ=30.4 ($C\underline{Me}_3$), 31.4 ($C\underline{Me}_3$), 35.1 ($\underline{C}Me_3$), 37.7 ($\underline{C}Me_3$), 43.1 ($CHBr_2$), 117.3 (arom.), 126.7 (arom.-CH), 127.0 (arom.-CH), 141.4 (arom.), 147.3 (arom.), and 150.6 (arom.); UV (hexane) 246 (sh, log ε 3.9), 283 (3.2), and 289 nm (3.2); IR (KBr) 1398, 1363, 1147, 1014, 734, and 673 cm^{-1}; MS *m/z* (rel intensity) 438 (M^+; 2), 361 (M^+-Br+2; 100), and 359 (M^+-Br; 52). Found: C, 41.07; H, 4.64%. Calcd for $C_{15}H_{21}Br_3$: C, 40.85; H, 4.80%.

2-Bromo-1,5-di-*t*-butyl-3-(methoxymethyl)benzene (3). A solution of sodium methoxide was prepared from 30 ml of absolute methanol (30 ml) and 0.92 g (40.0 mmol) of sodium. This solution was added to a solution of **1** (11.2 g, 32.8 mol) in methanol (125 ml) and was stirred at room temperature for 28 h. The methanol was replaced by ether and the solution was washed with water. After being dried with $MgSO_4$, the solvent was evaporated. The crude product was recrystallized from hexane to give 7.55 g of **3**. The filtrate was concentrated and chromatographed (SiO_2/hexane–CH_2Cl_2) to give 1.15 g of **3**. The combined yield of **3** was 85%. **3**: Colorless crystals; mp 45—46 °C (pentane); ^1H NMR δ=1.34 (9H, s, Bu^t), 1.56 (9H, s, Bu^t), 3.51 (3H, s, OMe), 4.57 (2H, s, CH_2O), 7.38 (1H, d, ^4J=2.5 Hz, arom.), and 7.44 (1H, d, ^4J=2.5 Hz, arom.); $^{13}C\{^1H\}$ NMR δ=30.1 ($C\underline{Me}_3$), 31.3 ($C\underline{Me}_3$), 34.7 ($\underline{C}Me_3$), 37.3 ($\underline{C}Me_3$), 58.6 (OMe), 75.6 (CH_2O), 120.2 (arom.), 123.7 (arom.-CH), 124.3 (arom.-CH), 138.5 (arom.), 147.2 (arom.), and 149.5 (arom.); UV (hexane) 220 (sh, log ε 4.1), 233 (sh, 3.8), and 265 nm (2.5); IR (KBr) 1369, 1362, 1198, and 1117 cm^{-1}; MS *m/z* (rel intensity) 312 (M^+; 45), 297 (M^+-Me; 100), 265 ($M^+-MeOCH_2+2$; 17), and 233 (M^+-Br; 13). Found: *m/z* 312.1084. Calcd for $C_{16}H_{25}BrO$: M, 312.1089. Found: C, 61.54; H, 7.84%. Calcd for $C_{16}H_{25}BrO$: C, 61.34; H, 8.04%.

2,4-Di-*t*-butyl-6-(methoxymethyl)phenylphosphonous Dichloride (4a). The bromobenzene **3** (67.6 mg, 0.216 mmol) in THF (8 ml) was lithiated with 0.223 mmol of butyllithium (1.59 M in hexane, 1 M=1 mol dm^{-3}) at −78 °C, then the solution was added to a THF (8 ml) solution of phosphorus trichloride (0.23 mmol) at this temperature. The resulting solution was warmed to 0 °C. An aliquot (ca. 0.2 ml) of the solution was removed to analyze, by ^{31}P NMR spectroscopy, indicating that only one single peak appeared due to 2,4-di-*t*-butyl-6-(methoxymethyl)phenylphosphonous dichloride (**4a**). Again, the reaction mixture was cooled to −78 °C, then methanol (2 ml) and triethylamine (0.05 ml) were added to this solution. The solution was stirred at this temperature for 5 min and was warmed up to room temperature. The ^{31}P NMR of the resulting solution also showed a single signal due to dimethyl 2,4-di-*t*-butyl-6-(methoxymethyl)phenylphosphonite (**5a**). The solvent was removed in vacuo and the residue was submitted to column chromatography (SiO_2/CH_2Cl_2) to give 10.5 mg (15%) of **5a**, 22.9 mg (34%) of methyl 2,4-di-*t*-butyl-6-(methoxymethyl)phenylphosphinate (**6a**), and 13.3 mg (26%) of 1,3-di-*t*-butyl-5-(methoxymethyl)benzene (**7**).

4a: ^1H NMR δ=1.34 (9H, s, Bu^t), 1.59 (9H, s, Bu^t), 3.47 (3H, s, $CH_2O\underline{Me}$), 5.14 (2H, s, CH_2), 7.43 (1H, dd, $^4J_{PH}$=6.6 Hz and $^4J_{HH}$=1.8 Hz, arom.), and 7.71 (1H, d, $^4J_{HH}$=1.8 Hz, arom.); MS *m/z* (rel intensity) 334 (M^+; 12), 299 (M^+-Cl; 100), 284 ($M^+-Cl-Me$; 24), 269 ($M^+-Cl-2Me$; 21), 242 ($M^+-Cl-Bu^t$; 16), and 57 (t-Bu^+; 19).

5a: Colorless oil; ^1H NMR δ=1.31 (9H, s, Bu^t), 1.58 (9H, s, Bu^t), 3.41 (3H, s, $CH_2O\underline{Me}$), 3.74 (6H, d, $^3J_{PH}$=14.2 Hz, POMe), 4.93 (2H, s, CH_2), 7.37 (1H, dd, $^4J_{PH}$=5.0 Hz and $^4J_{HH}$=2.0 Hz, arom.), and 7.58 (1H, d, $^4J_{HH}$=2.0 Hz, arom.); $^{31}P\{^1H\}$ NMR δ=185.5; $^{13}C\{^1H\}$ NMR δ=31.0 (s, *p*-$C\underline{Me}_3$), 33.6 (d, $^4J_{PC}$=19.4 Hz, *o*-$C\underline{Me}_3$), 34.8 (s, *p*-$\underline{C}Me_3$), 37.4 (d, $^3J_{PC}$=1.5 Hz, *o*-$\underline{C}Me_3$), 56.1 (d, $^2J_{PC}$=24.8 Hz, POMe), 57.9 (s, $CH_2O\underline{Me}$), 72.7 (d, $^3J_{PC}$=3.2 Hz, CH_2), 121.4 (d, $^3J_{PC}$=9.0 Hz, *m*-arom.), 123.7 (d, $^3J_{PC}$=0.8 Hz, *m'*-arom.), 135.0 (d, $^1J_{PC}$=29.1 Hz, *ipso*-arom.), 143.4 (s, *p*-arom.), 152.1 (d, $^2J_{PC}$=1.2 Hz, *o*-arom.), and 153.1 (d, $^2J_{PC}$=28.3 Hz, *o'*-arom.); UV (hexane) 233 (log ε 4.1), 275 (3.2), and 283 nm (3.1); IR (neat) 1103, 1045, 1020, and 727 cm^{-1}; MS *m/z* (rel intensity) 326 (M^+; 56), 311 (M^+-Me; 100), 295 (M^+-OMe; 27), 279 ($M^+-Me-OMe-1$; 84), 249 ($M^+-Me-2OMe$; 32), 93 $(P(OMe)_2^+$; 49), and 57 (t-Bu^+; 41). Found: *m/z* 326.1980. Calcd for $C_{18}H_{31}O_3P$: M, 326.2011.

6a: Colorless oil; ^1H NMR (600 MHz) δ=1.32 (9H, s, Bu^t), 1.53 (9H, s, Bu^t), 3.46 (3H, s, $CH_2O\underline{Me}$), 3.86 (3H, d, $^3J_{PH}$=12.3 Hz, POMe), 4.88 (1H, d, $^2J_{HH}$=13.0 Hz, CH_2), 4.92 (1H, d, $^2J_{HH}$=13.1 Hz, CH_2), 7.47 (1H, d, $^4J_{PH}$=6.2 Hz, arom.), 7.56 (1H, s, arom.), and 8.37 (1H, d, $^1J_{PH}$=567.5 Hz, PH); $^{13}C\{^1H\}$ NMR (150 MHz) δ=31.0 (s, $C\underline{Me}_3$), 33.6 (s, $C\underline{Me}_3$), 35.2 (s, $\underline{C}Me_3$), 36.8 (d, $^3J_{PC}$=2.8 Hz, *o*-$\underline{C}Me_3$), 53.3 (d, $^2J_{PC}$=6.4 Hz, POMe), 58.5 (s, $CH_2O\underline{Me}$), 72.7 (d, $^3J_{PC}$=6.8 Hz, CH_2), 122.8 (d, $^3J_{PC}$=13.6 Hz, *m*-arom.), 123.8 (d, $^1J_{PC}$=127.2 Hz, *ipso*-arom.), 124.1 (d, $^3J_{PC}$=10.9 Hz, *m'*-arom.), 144.1 (d, $^2J_{PC}$=5.8 Hz, *o*-arom.), 153.0 (d, $^2J_{PC}$=12.5 Hz, *o'*-arom.), and 154.9 (s, *p*-arom.); UV (hexane) 234 (log ε 4.2), 275 (3.3), and 283 nm (3.3); IR (neat) 1223, 1105, 1070, 1012, and 979 cm^{-1}; MS *m/z* (rel intensity) 312 (M^+; 15), 297 (M^+-Me; 33), 281 (M^+-MeO; 21), 265 ($MomxP^+$+1; 56), and 57 (t-Bu^+; 100). Found: *m/z* 312.1855. Calcd for $C_{17}H_{29}O_3P$: M, 312.1854.

7: Colorless oil; ^1H NMR δ=1.39 (18H, s, Bu^t), 3.47 (3H, s, OMe), 4.50 (2H, s, CH_2), 7.24 (2H, d, ^4J=1.7 Hz, arom.), and 7.43 (1H, t, ^4J=1.7 Hz, arom.); $^{13}C\{^1H\}$ NMR δ=31.5 ($C\underline{Me}_3$), 34.8 ($\underline{C}Me_3$), 58.2 (OMe), 75.5 (CH_2), 121.7 (arom.-CH), 122.0 (arom.-CH), 137.2 (arom.), and 150.8 (arom.); UV (hexane) 214 (log ε 4.1), 259 (sh, 2.5), 264 (2.5), and 273 nm (sh, 2.3); IR (neat) 1600, 1477, 1363, 1247, 1197, 1105, 865, and 713 cm^{-1}; MS *m/z* (rel intensity) 234 (M^+; 12), 219 (M^+-Me; 100), 203 (M^+-MeO; 17), 177 (M^+-Bu^t; 16), and 57 (t-Bu^+; 16). Found: *m/z* 234.1982. Calcd for $C_{16}H_{26}O$: M, 234.1984.

5,7-Di-*t*-butyl-2,1-oxaphosphaindan 1-Oxide (9). The phosphonous dichloride **4a** was prepared below 0 °C from 89.3 mg (0.285 mmol) of **3** in THF (5 ml) according

to the method described above. The solution was allowed to warm to room temperature and stirred for 10 h. The ^{31}P NMR spectrum of the resulting solution showed a single signal due to 5,7-di-*t*-butyl-1-chloro-2,1-oxaphosphaindan (**8**). The formation of chloromethane was indicated by the ^{1}H NMR spectrum of the solution, which showed a peak due to CH_3Cl at δ=3.00 besides the signals due to **8**. To this solution was added 10 ml of water. The mixture was extracted twice with 30 ml of ether and dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed (SiO_2/Et_2O) to give 24.1 mg (32%) of **9**.

8: ^{1}H NMR δ=1.35 (9H, s, Bu^t), 1.55 (9H, d, $^{5}J_{PH}$=0.5 Hz, Bu^t), 5.36 (1H, dd, $^{3}J_{PH}$=19.7 Hz and $^{2}J_{HH}$=14.2 Hz, CH_2), 5.65 (1H, dd, $^{3}J_{PH}$=7.1 Hz and $^{2}J_{HH}$=14.2 Hz, CH_2), 7.29 (1H, m, arom.), and 7.47 (1H, m, arom.); ^{31}P{^{1}H} NMR δ=180.8; MS *m/z* (rel intensity) 286 (M^++2; 29), 284 (M^+; 100), 269 (M^+−Me; 69), 249 (M^+−Cl; 69), 233 (M^+−Cl−O; 69), 224 (79), and 57 (*t*-Bu$^+$; 35). Found: *m/z* 284.1105. Calcd for $C_{15}H_{22}ClOP$: M, 284.1097.

9: Colorless powder; mp 285—287 °C (hexane); ^{1}H NMR δ=1.34 (9H, s, Bu^t), 1.55 (9H, s, Bu^t), 5.26 (1H, dd, $^{2}J_{HH}$=13.6 Hz and $^{3}J_{PH}$=11.3 Hz, CH_2), 5.50 (1H, d of pseudo t, $^{2}J_{HH}$=13.6 Hz and $^{3}J_{PH}$=$^{4}J_{HH}$=2.6 Hz, CH_2), 7.17 (1H, s, arom.), 7.53 (1H, d, $^{4}J_{PH}$=6.1 Hz, arom.), and 8.30 (1H, dd, $^{1}J_{PH}$=595.2 Hz and $^{4}J_{HH}$=2.3 Hz, PH); ^{31}P NMR δ=42.2 (d, $^{1}J_{PH}$=595.5 Hz); ^{13}C{^{1}H} NMR (150 MHz) δ=31.1 (s, C$\underline{\text{Me}}_3$), 31.7 (s, C$\underline{\text{Me}}_3$), 35.4 (s, $\underline{\text{C}}$Me$_3$), 37.2 (s, $\underline{\text{C}}$Me$_3$), 72.0 (s, CH_2), 116.4 (d, $^{3}J_{PC}$=11.2 Hz, *m*-arom.), 122.1 (d, $^{1}J_{PC}$=114.7 Hz, *ipso*-arom.), 123.9 (d, $^{3}J_{PC}$=11.3 Hz, *m'*-arom.), 145.8 (d, $^{2}J_{PC}$=21.9 Hz, *o*-arom.), 154.6 (d, $^{2}J_{PC}$=11.5 Hz, *o'*-arom.), and 157.3 (d, $^{4}J_{PC}$=2.5 Hz, *p*-arom.); UV (hexane) 222 (log ε 4.0), 260 (sh, 2.8), 270 (3.0), and 278 nm (3.1); IR (KBr) 2413 and 1230 cm^{-1}; MS *m/z* (rel intensity) 266 (M^+; 23), 251 (M^+−Me; 100), 224 (50), and 57 (*t*-Bu$^+$; 11). Found: *m/z* 266.1444. Calcd for $C_{15}H_{23}O_2P$: M, 266.1436.

1-[2,4-Di-*t*-butyl-6-(methoxymethyl)phenyl]-2-(2,4,6-tri-*t*-butylphenyl)diphosphene (10a). The phosphonous dichloride **4a** was prepared from 90.1 mg (0.287 mmol) of **3** in THF (8 ml) according to the method described above and the resulting solution was cooled to −78 °C. To this solution was added a THF (8 ml) solution of lithium 2,4,6-tri-*t*-butylphenylphosphide[12] (0.287 mmol) at this temperature. DBU (0.06 ml, 0.40 mmol) was added to the resulting mixture and the solution was warmed up to room temperature. Then the solvent was removed in vacuo. The ^{31}P NMR spectrum of the residue indicated the formation of the diphosphene **10a** as a major product. Crude diphosphene **10a** was obtained by flash column chromatography (SiO_2/pentane–Et_3N), however, attempted further purification of **10a** was not successful because of the decomposition: ^{1}H NMR (C_6D_6) δ=1.26 (9H, s, Bu^t), 1.29 (9H, s, Bu^t), 1.31 (9H, s, Bu^t), 1.55 (18H, s, *o*-Bu^t), 3.23 (3H, s, OMe), 4.81 (2H, s, CH_2), 7.44 (2H, s, Ar-H), 7.61 (1H, bs, Momx-H), and 7.93 (1H, bs, Momx-H); UV (hexane) 226 (sh, log ε 4.4), 276 (4.0), 326 (3.6), and 466 nm (2.5); MS *m/z* (rel intensity) 540 (M^+; 4), 483 (M^+−Bu^t; 27), 277 (ArP$^+$+1; 100), and 57 (*t*-Bu$^+$; 45). Found: *m/z* 540.3655. Calcd for $C_{34}H_{54}OP_2$: M, 540.3650.

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