Heteroatom Chemistry
Volume 9, Number 7, 1998

Synthesis and Photolysis of Phosphiranes and Diphosphiranes Carrying Sterically Protecting Groups on the Phosphorus Atoms

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Received 14 November 1997; revised 18 February 1998

ABSTRACT: *Phosphiranes and diphosphiranes carrying the 2,4,6-tri-t-butylphenyl or 2,6-dimesityl-4-methylphenyl group were synthesized to serve as anticipated phosphinidene-precursors, and their photolyses were investigated by means of ^{31}P and ^{1}H NMR, and EPR spectroscopy. Photolysis of the diphosphirane possessing the 2,4,6-tri-t-butylphenyl group on the phosphorus atoms at ambient temperature proceeded selectively to give the phosphaindan and phosphaethene derivatives. A phosphorus-centered radical was observed in an EPR study of the photolysis at cryogenic temperature, but neither the triplet phosphinidene nor triplet carbene was detected. The 2,4,6-tri-t-butylphenylphosphirane derivatives, which exclusively afforded the phosphaindan by irradiation at room temperature, also generated the same phosphorus-centered radical by the photolysis at cryogenic temperature. A novel 2,6-dimesityl-4-methylphenylphosphirane was synthesized to avoid intramolecular reaction with the ortho substituent, but introduction of the 2,6-dimesityl-4-methylphenyl group in place of the 2,4,6-tri-t-butylphenyl group dramatically decreased the photoreactivity. Thus, photolysis of the phosphirane resulted in recovery of the starting material. Participation of the ortho t-butyl group can therefore be regarded as a key feature of the photolysis.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 607–613, 1998

INTRODUCTION

It is one of the most interesting topics in current phosphorus chemistry to investigate the generation, reaction, and direct observation of a phosphinidene, the phosphorus counterpart of a nitrene [1]. Phosphinidenes have quite often been referred to as reaction intermediates to explain reactions such as photolysis of phospholenes [2], polyphosphanes [3], phosphiranes [2], diphosphenes [4], phosphorus(III) diazides [5], and phosphaketenes [5]. On the other hand, although recent theoretical studies [6] have predicted phenylphosphinidene to be a ground-state triplet molecule similar to phenylnitrene, only a few reports of direct observation have been made. Indeed, the only example in the literature that deals with an EPR observation of a triplet phosphinidene, that is, mesitylphosphinidene, is that reported by Li et al. [7]. In our early study of bis(2,4,6-tri-*t*-butylphenyl)diphosphene, **1**, we reported the formation of phosphaindan **2** by UV irradiation of **1**, which corresponds to a formal C–H insertion product of 2,4,6-tri-*t*-butylphenylphosphinidene **3** (Scheme 1) [4], as well as *E*/*Z* isomerization of **1** brought about by visible light irradiation [8]. The formation of phosphaindan **2** was also observed in the photolysis of the so-called 2,4,6-tri-*t*-butylphenylphosphinidene precursors, such as phospholenes [2], phosphiranes [2], phosphorus(III) diazides [5], and phosphaketenes [5], carrying the 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar in Scheme 1); thus, the phosphinidene intermediates have been suggested. In this article, we describe the syntheses and photolyses of

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Dedicated to Prof. Robert R. Holmes on the occasion of his seventieth birthday.

CCC 1042-7163/98/070607-07

phosphiranes **4a, 4b,** and **5** and the diphosphirane **6,** each carrying the 2,4,6-tri-*t*-butylphenyl or 2,6-dimesityl-4-methylphenyl groups. At the beginning of this work, attempts were made to observe triplet 2,4,6-tri-*t*-butylphenylphosphinidene **3** directly by EPR spectroscopy. However, in the course of our study, the significance of participation of the *ortho t*-butyl substituents became clear, and we therefore desired to study the behavior of a sterically protecting group with comparable bulkiness but less reactivity as compared with the 2,4,6-tri-*t*-butylphenyl group. Recently, we [9] and others [10] have reported the application of the 2,6-diarylphenyl–type of sterically protecting group, which can easily be synthesized by the Hart reaction [11], and such protecting groups have been successfully used for stabilizing low-coordinated main-group element as well as transition metal compounds, as reported by He et al. [12], for diphosphenes and a phosphaarsene. Thus, we prepared 2,6-dimesityl-4-methylphenylphosphirane **5** as a possible phosphinidene precursor bearing a protecting group with less reactivity. Furthermore, in this article, the formation of reaction intermediates of photolysis of 2,4,6-tri-*t*-butylphenylphosphiranes and diphosphiranes is discussed based on EPR studies carried out at cryogenic temperatures.

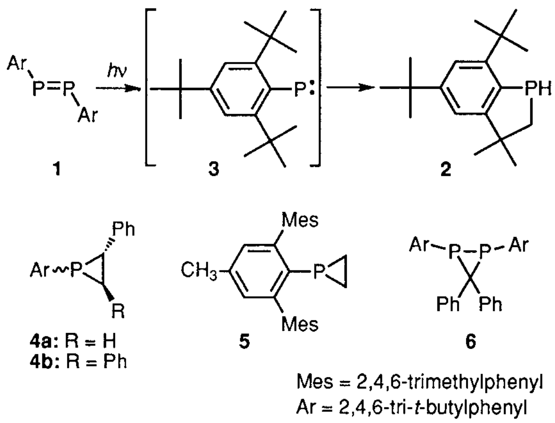
RESULTS AND DISCUSSION

Synthesis

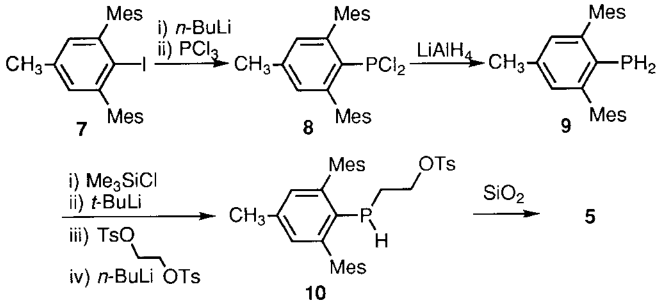
1-(2,4,6-Tri-*t*-butylphenyl)-2-phenylphosphirane (**4a**) [13], and 1,2-bis(2,4,6-tri-*t*-butylphenyl)-3,3-diphenyldiphosphirane (**6**) [14] were synthesized according to the literature methods. 1-(2,4,6-Tri-*t*-butylphenyl)-2,3-diphenylphosphirane (**4b**) was prepared by the reaction of lithium trimethylsilyl(2,4,6-tri-*t*-butylphenyl)phosphide with *trans*-stilbene oxide. 2,6-Dimesityl-4-methylphenylphosphirane (**5**) was synthesized to estimate the influence of the *ortho t*-butyl substituent in the photolysis (see later). 2,6-Dimesityl-4-methyliodobenzene (**7**), which was prepared according to Hart's procedure [11], was lithiated with butyllithium and allowed to react with phosphorus trichloride to give the dichlorophosphine **8** [9,10]. The dichlorophosphine **8** was converted to the air-stable primary phosphine **9** by $LiAlH_4$ reduction. According to the procedure of Oshikawa and Yamashita [15] for the preparation of 2,4,6-tri-*t*-butylphenylphosphiranes, a reaction sequence of lithiation of **9** followed by the reaction with ethylene glycol ditosylate and cyclization by the action of butyllithium, was attempted, but a significant amount of 1,2-bis(2,6-dimesityl-4-methylphenyl)diphosphane ($\delta_P = -101$ and -111) [16] was formed in addition to tosylate **10,** the desired intermediate. On the other hand, the successive addition of chlorotrimethylsilane, *t*-butyllithium, ethylene glycol di-*p*-tosylate, and butyllithium to **9** suppressed the formation of the above-mentioned by-product and afforded the tosylate **10** in a moderate yield (Scheme 2). Although the cyclization of the tosylate **10** to the phosphirane **5** with butyllithium was not effective, **10** was accidentally converted to **5** by passing a solution of **10** through a silica-gel column. Attempted synthesis of 1-(2,6-dimesityl-4-methylphenyl)-2-phenylphosphirane was not successful either by the procedure of Oshikawa and Yamashita [15] or by ours [13], but the reaction of bis(2,6-dimesityl-4-methylphenyl)diphosphene (**17**) [9,10] with excess diphenyldiazomethane afforded the corresponding diphosphirane, although only in a trace amount.

Photolysis at Room Temperature

Benzene-d_6 solutions of phosphiranes **4a, 4b,** and **5** and diphosphirane **6** were irradiated with a Xe lamp through a cut filter ($\lambda > 300$ nm) at room temperature, and the reactions were monitored by ^1H and ^{31}P

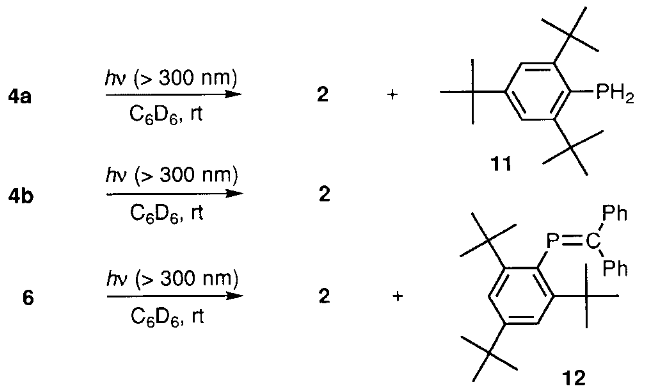


SCHEME 1



SCHEME 2

NMR spectroscopy. Photolysis of phosphiranes **4a** and **4b** led to almost exclusive formation of the phosphaindan **2**, with but a trace amount of 2,4,6-tri-*t*-butylphenylphosphine (**11**) also being formed, which is consistent with the reported results of photolysis of other phosphiranes carrying the 2,4,6-tri-*t*-butylphenyl group [2]. Irradiation ($\lambda > 300$ nm) of the diphosphirane **6** gave phosphaethene **12** and phosphaindan **2** in almost a combined quantitative yield. Diphosphene **1** and other products, such as tetraphenylethene, were not detected. These results suggest selective bond cleavage at the weaker P–P and P–C bonds (Scheme 3). The photolysis in benzene-d_6 resulted in nonincorporation of any deuteriums into **2**. On the other hand, irradiation of 2,6-dimesityl-4-methylphenylphosphirane (**5**) resulted only in the recovery of **5**. Introduction of the 2,6-dimesityl-4-methylphenyl group in place of the 2,4,6-tri-*t*-butylphenyl group significantly decreased the photoreactivity.



SCHEME 3

Photolysis at a Cryogenic Temperature

In an attempt to observe the signals attributable to intermediates of the photolysis described earlier, the poly(methyl methacrylate) (PMMA) or methylcyclohexane matrices of phosphiranes **4a**, **4b** and **5** and diphosphirane **6** were irradiated in an EPR cavity at a cryogenic temperature.

EPR spectra, collected after the photolysis of phosphiranes **4a**, **4b**, and diphosphirane **6** in a PMMA matrix at 77 K, which gave the phosphaindan **2** at room temperature, as mentioned earlier, consisted in each case of the identical signals of a typical phosphorus-centered radical, superimposed on those due to photolysis of PMMA itself. A typical EPR spectrum obtained after the photolysis of **6** is shown in Figure 1. Large $a_{\parallel}(\mathrm{P}) = 26.2$ mT at $g_{\parallel} = 2.0015$ and small $a_{\perp}(\mathrm{P}) = 6.3$ mT at $g_{\perp} = 2.0038$ values with a calculated isotropic coupling constant ($a_{iso} = 12.9$ mT) are characteristic of divalent neutral phosphorus radicals with axial symmetry [17,18], and the small splitting, probably attributable to the isotropic hyperfine coupling with a hydrogen atom [$a(\mathrm{H}) = 2.3$ mT] attached directly to the phosphorus atom [18], was observed for the signals at the highest and lowest fields. Other signals, such as $\Delta m_s = 2$, typical of triplet carbenes [20] and phosphinidenes [7], were not detected from 3 to 1500 mT. Absence of the signals of triplet carbene is consistent with the results of the photolysis carried out at room temperature. Photolysis of **1** and **4a** at 5 K with scanning up to 1500 mT was carried out to judge whether the triplet phosphinidene intermediate was involved or not. However, no signals other than those observed at 77 K, with less resolution and intensity, were detected [21]. Although the formation of the phosphaindan **2** at room temperature suggests the existence of triplet phosphinidene and/or triplet biradicals as intermediates observable by EPR, the signals should not be attributed to triplet biradicals but to a doublet phosphorus-centered radical, such as **15**. The triplet phosphinidene would show a signal in a very high field such as those observed for nitrenes. On the other hand, the biradicals **14a**, **14b**, **14c**, and **16** should have significant *D* values (>30 mT) due to the existence of short distances (<4.3 Å) between radical centers, taking the point-dipole approximation into account (Schemes 4 and 5). Thus, their EPR spectra would consist of more complex signals due to large fine structures (*D*) and comparable hyperfine structures [*a*(P)] in wider range, and

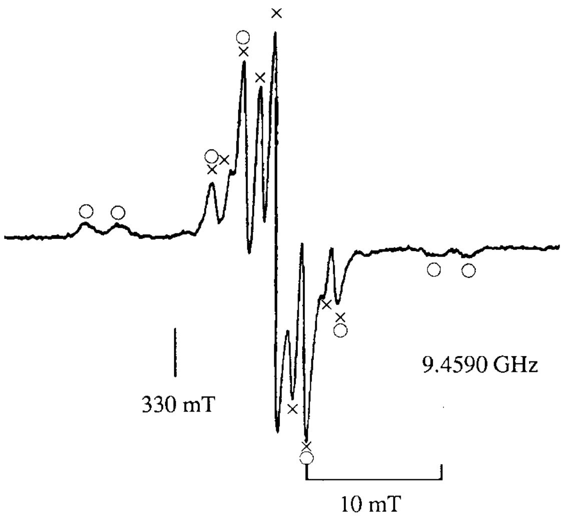
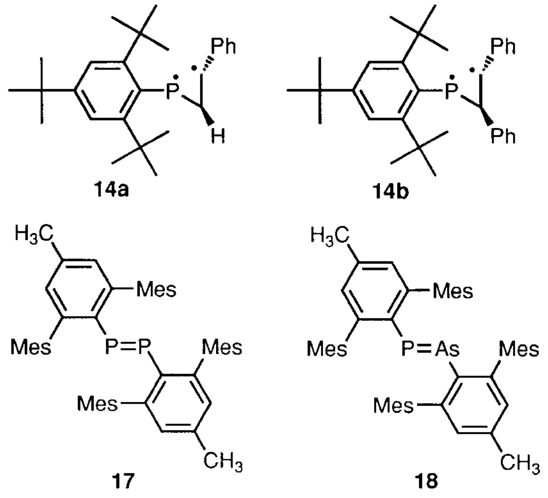
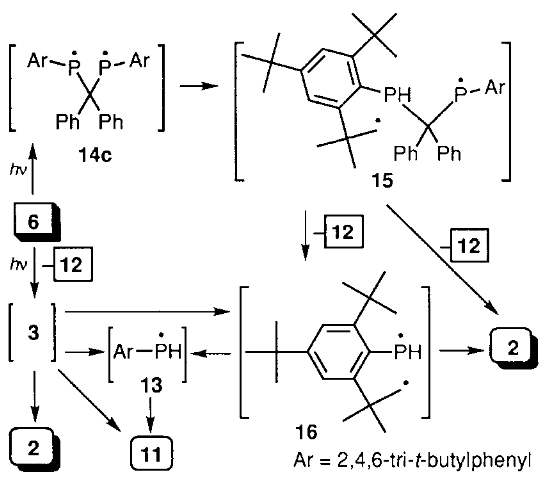


FIGURE 1 EPR spectrum obtained after the photolysis of **6** in a PMMA matrix at 77 K. o: Signals due to the phosphorus-centered radical. x: Signals derived from photolysis of PMMA.



SCHEME 4



SCHEME 5

$\Delta m_s = 2$ signals would be observed [23]. Although the signals of a carbon-centered radical moiety, which are expected to be apparent around $g = 2.002$ with $a(\mathrm{H}) = 2$–3 mT [19], could be overlapped on the signals from the matrix, expected short distances between radical centers do not support negligible or smaller exchange interaction relative to the hyperfine coupling. Assignment to **14** or **15** is also excluded for the reason that **4a, 4b,** and **6** gave the identical EPR spectra. Thus, we assigned the observed signals as being those of a phosphorus radical **13** that are responsible for the formation of small amount of **11** rather than **2.** On the other hand, no EPR signals, except for those due to decomposition of the matrix, were observed after photolysis of **5** in a methylcyclohexane matrix at 77 K.

Similar differences of photoreactivity between the 2,4,6-tri-*t*-butylphenyl and the 2,6-dimesityl-4-methylphenyl derivatives were also observed in the photolysis of bis(2,6-dimesityl-4-methylphenyl)-diphosphene (**17**) and bis(2,6-dimesityl-4-methylphenyl)phosphaarsene (**18**) [9]. Irradiation of the diphosphene **17** and the phosphaarsene **18** resulted in recovery of the starting materials, and no products, including *Z*-isomers, were observed. Enhanced reactivity of the 2,4,6-tri-*t*-butylphenyl derivatives could be explained by the geometry of the molecules wherein the distance between the phosphorus atom and the hydrogen atom of the *ortho*-*t*-butyl group could be close to that of the phosphorus–hydrogen bond length (1.4 vs. 1.5 Å). Therefore, reactive intermediates, such as the phosphinidene **3** or the photoexcited **6** or the biradical **14c** (depicted in Scheme 5), would be expected to abstract the closest hydrogen atom to generate a carbon radical center near the phosphorus atom. The carbon radical center would intramolecularly attack the phosphine to give **2.** As a reaction path of the photolysis of phosphiranes **4a, 4b,** and the diphosphirane **6,** possessing the 2,4,6-tri-*t*-butylphenyl group, we could assume several possible paths, including the formation of intermediates observable by EPR (Scheme 5 for **6**), such as a triplet phosphinidene **3**, biradicals **14a, 14b, 14c,** and **16.** However, the absence of EPR signals due to the triplet phosphinidene or biradicals excludes intermediates stable enough to be observed by EPR under the matrix isolated conditions, although the EPR spectrum and ground-state multiplicity of phosphinidenes have not been fully established. Thus, intermediates for the formation of phosphaindan **2** could be the singlet or very short-lived species if they exist. No incorporation of deuterium into **2** suggests a very fast intramolecular cyclization. Thus, the species observed in the EPR studies represents only a minor contribution, although the signals are characteristic for the 2,4,6-tri-*t*-butylphenyl derivatives, and the *ortho*-*t*-butyl substituent located close to the phosphorus atom seems to play an important role, this also being consistent with the low photoreactivity of the 2,6-dimesityl-4-methylphenyl derivatives.

EXPERIMENTAL

General

^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AC200P or an AM600 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are expressed as δ down field from external tetramethylsilane. ^{31}P NMR chemical shifts are expressed as δ down field from external 85% H_3PO_4. X-band EPR spectra were measured on a Bruker ESP300E spectrometer equipped with a JEOL ES-UCD2X liquid nitrogen Dewar or an Oxford ESR900 continuous-flow liquid helium cryostat. Infrared spectra and ultraviolet-visible spectra were collected on a Horiba FT-300 spectrometer and a Hitachi U-3210 spectrophotometer, respectively. In the photolysis, samples were degassed by threefold freeze-and-thaw cycles and irradiated with an Ushio UXL500D-O Xe lamp in a Model UI501C lamp house using cut filters. Mass spectra were measured on a Hitachi M-2500S or a JEOL HX-100 instrument with electron impact (EI) ionization at 70 eV or a JEOL HX-110 with fast atom bombardment (FAB) ionization using an *m*-nitrobenzyl alcohol matrix. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Graduate School of Science, Tohoku University. Column chromatography was carried out using compressed air over silica gel (Fuji Silysia, BW-300) unless specified otherwise. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under argon just prior to use. 1-(2,4,6-Tri-*t*-butylphenyl)-2-phenylphosphirane [13] and 1,2-bis(2,4,6-tri-*t*-butylphenyl)-3,3-diphenyldiphosphirane [14] were synthesized according to the literature methods.

Synthesis

2,3-Diphenyl-1-(2,4,6-tri-t-butylphenyl)phosphirane (**4b**). Butyllithium (0.21 mL, 1.68 M in hexane) was added to a solution of 2,4,6-tri-*t*-butylphenylphosphine (100 mg, 0.36 mmol) in THF (5 mL) at 0°C, and the mixture was stirred for 20 minutes, then chlorotrimethylsilane (0.046 mL, 0.36 mmol) was added dropwise. After 15 minutes, butyllithium (0.26 mL, 1.68 M in hexane) was added, again at 0°C, and the mixture was stirred for 15 minutes. The resulting silylphosphide was allowed to react with *trans*-stilbene oxide (106 mg, 0.54 mmol) at -78°C for 10 minutes in the dark, and the mixture was stirred for 12 hours at room temperature. The THF solution was directly submitted to flash chromatography (silica gel, hexane) to give 80.8 mg (49%) of **4b. 4b:** colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.20 (9H, s), 1.34 (9H, s), 1.57 (9H, s), 2.72 (1H, dd, J_{PH} = 24.1 Hz, J_{HH} = 8.6 Hz), 2.96 (1H, dd, J_{HH} = 8.6 Hz, J_{PH} = 2.6 Hz), 6.01 (2H, d, J = 7.4 Hz), 6.87 (2H, t, J = 7.7 Hz), 6.91–6.93 (1H, m), 6.94 (1H, tm, J = 7.3 Hz), 7.18 (1H, tm, J = 7.3 Hz), 7.20 (2H, dm, J = 7.3 Hz), 7.29 (2H, tm, J = 7.7 Hz), and 7.43 (1H, br.s); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 31.5, 33.6 (d, $^{4}J_{PC}$ = 10.0 Hz), 34.2 (d, $^{4}J_{PC}$ = 6.3 Hz), 34.5, 38.6, 39.5, 40.1 (d, $^{1}J_{PC}$ = 36.8 Hz), 43.9 (d, $^{1}J_{PC}$ = 49.8 Hz), 122.1, 123.5, 125.2, 125.7, 126.8 (d, $^{3}J_{PC}$ = 8.0 Hz), 127.2, 127.3, 128.4, 128.9 (d, $^{1}J_{PC}$ = 65.6 Hz), 138.7, 142.3 (d, $^{2}J_{PC}$ = 8.7 Hz), 148.6, 157.2 (d, $^{2}J_{PC}$ = 8.0 Hz), 158.0; ^{31}P NMR (81 MHz, $CDCl_3$) δ = -119.8 (d, $^{2}J_{PH}$ = 24.0 Hz); UV-vis (hexane) λ (log ε) 227 (sh, 4.44), 260 (4.26) nm; IR (neat) ν 3084, 3060, 3026, 2954, 2929, 2868, 1734, 1597, 1527, 1495, 1471, 1394, 1363, 1282, 1242, 1209, 1188, 1126, 1074, 1030, 974, 901, 877, 823, 754, 698, and 673 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity) 456 (M^+; 0.5%), 441 (M^+-15; 0.2), 399 (M^+-57; 0.2), 276 (M^+-180; 88), 261 (M^+-195; 37), 220 (M^+-236; 91), 205 (M^+-251; 31), and 57 (100). Found: *m/z* 456.2938. Calcd for $C_{32}H_{41}P$: M, 456.2946.

2,6-Dimesityl-4-methyliodobenzene (**7**). To a stirred mesitylmagnesium bromide solution [prepared from mesityl bromide (5.40 mL, 35.3 mmol) and magnesium (941 mg, 38.7 mmol) in THF (70 mL)] was added dropwise 2,6-dibromo-4-methyliodobenzene (3.31 g, 8.80 mmol) in THF (30 mL) over a period of 1 hour at room temperature. After having been stirred for 4 hours, the reaction mixture was cooled in an ice bath and iodine (7.47 g, 29.4 mmol) in THF (18 mL) was added. The mixture was stirred vigorously and warmed to room temperature. The excess amount of iodine was reduced with an aqueous $NaHSO_3$ solution, and the products were extracted several times with ether, washed with aqueous $NaHCO_3$ and saturated NaCl solutions, and dried over $MgSO_4$. After removal of the solvent, a small amount of hexane was added. Analytically pure crystals of **7** (1.71 g, 3.76 mmol, 43%) that separated from the residue were collected by filtration. The filtrate was submitted to flash column chromatography (silica gel, hexane) to give 815 mg (1.79 mmol, 20%) of **7. 7:** colorless prisms (hexane–benzene), mp 218.5–219.0°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.99 (12H, s), 2.35 (9H, s), 6.91 (2H, s), and 6.95 (4H, s); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 20.2, 21.0, 21.2, 103.3, 128.0, 128.6, 135.3, 137.0, 138.6, 142.0, and 146.8; IR (KBr) ν 3022, 2968, 2941, 2910, 2852, 2729, 1610, 1568, 1481, 1444, 1390, 1331, 1036, 1007, 854, 848, 789, 744, 590, and 552 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity) 454 (M^+; 100%), 327 (M^+-127; 9), 312 (M^+-142; 9), and 297 (M^+-157; 4). Found: C, 65.83; H, 6.17; I, 27.85%. Calcd for $C_{25}H_{27}I$: C, 66.08; H, 5.99; I, 27.93%.

Dichloro-(2,6-dimesityl-4-methylphenyl)phosphine (**8**). Butyllithium (1.44 mL, 1.68 M in hexane) was added to a solution of **7** (1.00 g, 2.20 mmol) in THF (30 mL) at -78°C, and the mixture was stirred for 1.5 hours. Then phosphorus trichloride (0.58 mL, 6.65 mmol) was added at -78°C. The reaction mixture was stirred at -78°C for 15 minutes and refluxed for 1.5 hours. After the solvent and the excess amount of phosphorus trichloride had been removed in vacuo, the residue was extracted with ether and washed with cold water and a saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated to yield **8** almost quantitatively as a pale yellow solid. **8:** ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 2.04$ (12H, s), 2.34 (6H, s), 2.41 (3H, s), and 6.92 (6H, s), ^{31}P NMR (81 MHz, $CDCl_3$) $\delta = 161.2$ (s).

2,6-Dimesityl-4-methylphenylphosphine (**9**). A solution of **8** (314 mg, 0.73 mmol) in ether (10 mL) was added to a suspension of $LiAlH_4$ (40.3 mg, 1.06 mmol) in ether (1.5 mL) in 5 minutes at 0°C with stirring, and the mixture was refluxed for 1 hour. A small amount of water was added slowly to decompose the excess $LiAlH_4$. The mixture was extracted with ether, washed with cold water and a saturated NaCl solution, and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography [silica gel, hexane to hexane/benzene (5:1, v/v)] to give 221 mg (84%) of **9**. **9:** colorless prisms (hexane), mp 212.5–213.5°C; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 2.03$ (12H, s), 2.36 (6H, s), 2.39 (3H, s), 3.05 (2H, d, $^1J_{PH} = 209.8$ Hz), 6.91 (2H, br.d, $J = 2.0$ Hz), and 6.98 (4H, s); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) $\delta = 20.2$ (d, $^5J_{PC} = 1.4$ Hz), 21.1, 21.2, 125.7 (d, $^1J_{PC} = 6.5$ Hz), 128.2, 128.5 (d, $^3J_{PC} = 1.8$ Hz), 135.5, 136.8, 138.0, 139.2 (d, $^3J_{PC} = 2.8$ Hz), and 145.2 (d, $^2J_{PC} = 11.6$ Hz); ^{31}P NMR (81 MHz, $CDCl_3$) $\delta = -147.2$ (t, $^1J_{PH} = 209.8$ Hz); IR (KBr) ν 3024, 2968, 2941, 2912, 2854, 2729, 2362, 2318, 2299, 1610, 1556, 1479, 1441, 1375, 1066, 1036, 1011, 856, 741, and 561 cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 360 (M^+; 29%), 345 (M^+-15; 100), 328 (M^+-32; 6), and 313 (M^+-47; 4). Found: m/z 360.2024. Calcd for $C_{25}H_{29}P$: M, 360.2007. Found: C, 83.21; H, 8.26%. Calcd for $C_{25}H_{29}P$: C, 83.30; H, 8.11%.

1-(2,6-Dimesityl-4-methylphenyl)phosphirane (**5**). *t*-Butyllithium (0.30 mL, 1.46 M in pentane) was added to a solution of **9** (150 mg, 0.42 mmol) and chlorotrimethylsilane (0.056 mL, 0.44 mmol) in THF (7.5 mL) at −78°C, and the mixture was stirred for 20 minutes. A solution of ethylene glycol di-*p*-tosylate (185 mg, 0.50 mmol) in THF (7.5 mL) was added over a period of 5 minutes at −78°C, then butyllithium (0.28 mL, 1.56 M in hexane) was added, and the mixture was stirred at −78°C for 15 minutes. After the mixture had been stirred at room temperature overnight, butyllithium (0.28 mL, 1.56 M in hexane) was added again at −78°C to promote the conversion to tosylate **10** (with use of ^{31}P NMR monitoring). The reaction mixture was stirred for 30 minutes at −78°C and for 3 hours at room temperature. After removal of the solvent, the residue was passed through a silica-gel column (Merck, Kieselgel 60G, hexane), and formation of **5** was confirmed by ^{31}P NMR spectroscopy. The solution was concentrated and the residue was chromatographed (silica gel, hexane) to give 66.6 mg (41%) of **5**. **5:** colorless solid, mp 163.0–166.0°C; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 0.3$–1.0 (4H, m), 2.18 (12H, s), 2.39 (3H, s), 2.42 (6H, s), 6.86 (2H, s), and 7.05 (4H, s); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) $\delta = 8.4$ (d, $^1J_{PC} = 39.8$ Hz), 21.0 (d, $^5J_{PC} = 4.9$ Hz), 21.2, 128.4, 129.5 (d, $^3J_{PC} = 0.5$ Hz), 134.0 (d, $^1J_{PC} = 42.8$ Hz), 135.4, 136.5, 138.0, 139.3 (d, $^3J_{PC} = 2.3$ Hz), and 146.5 (d, $^2J_{PC} = 10.8$ Hz); ^{31}P NMR (81 MHz, $CDCl_3$) $\delta = -229.4$ (t, $^2J_{PH} = 16.7$ Hz); UV-vis (hexane) λ (log ε) 218 (sh, 4.68), 245 (sh, 4.30) nm; IR (KBr) ν 2995, 2960, 2941, 2918, 2856, 2731, 1728, 1608, 1593, 1550, 1479, 1446, 1377, 1281, 1271, 1120, 1045, 1034, 987, 962, 879, 870, 850, 783, 640, and 559 cm^{-1}; MS (EI, 70 eV) m/z (rel. intensity) 386 (M^+; 3%), 358 (M^+-28; 100), 343 (M^+-43; 31), 327 (M^+-59; 3), and 313 (M^+-73; 7). Found: m/z 386.2172. Calcd for $C_{27}H_{31}P$: M, 386.2163.

ACKNOWLEDGMENTS

Financial support by Tokuyama Science Foundation and Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture (Numbers 08454193 and 09239101) are gratefully acknowledged. Shin-Etsu Chemical Co. is also gratefully appreciated for donation of silicon chemicals. This work was partially carried out in the Advanced Instrumental Laboratory for Graduate Research of Department of Chemistry, Graduate School of Science, Tohoku University.

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