

Preparation and ^{31}P NMR Study of Some Low-Coordinated Organophosphorus Compounds Bearing the 2,4-Di-*t*-butyl-6-isopropylphenyl Group

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ABSTRACT: 2-Bromo-1,5-di-*t*-butyl-3-isopropylbenzene was prepared and converted to the 2,4-di-*t*-butyl-6-isopropylphenyl-substituted phosphonous dichloride, primary phosphine, diphosphenes, and dithioxophosphorane. The ^{31}P NMR chemical shifts of these compounds are close to those of 2,4-di-*t*-butyl-6-methylphenyl substituted congeners. © 2001 John Wiley & Sons, Inc. *Heteroatom Chem* 12:418–423, 2001

INTRODUCTION

Kinetic stabilization of compounds containing heavier main group elements, by use of bulky substituents, are of current interest [1–3]. The 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Mes*) is one of the typical and powerful bulky protecting groups, and, by utilizing this substituent, we and others have successfully prepared various types of

phosphorus compounds of unusual structures, such as diphosphenes [4], phosphacumulenes [5–11], phospharadialenes [12], and phosphaquinoxones [13,14]. In the course of our continuing effort of developing new stabilizing groups and fine tuning of the stabilizing abilities of the substituents, we have examined various stabilizing groups such as 2,4-di-*t*-butyl-6-methylphenyl (abbreviated to Dbt) [15,16], 2,4-di-*t*-butyl-6-(dimethylamino)phenyl (abbreviated to Mx) [17–19], 2,4-di-*t*-butyl-6-methoxyphenyl (abbreviated to Mox) [20–22], and 2,4-di-*t*-butyl-6-[1,1-dimethyl-2-(dimethylamino)ethyl]phenyl [23] groups.

Among these substituents, application of the 2,4-di-*t*-butyl-6-isopropylphenyl group (hereafter abbreviated to Px) for this purpose has not been reported. In order to get information about the structure–properties relationship (for example, structure–NMR chemical shift relationship) among low-coordinated phosphorus compounds, such as diphosphenes, it is worthwhile to prepare compounds expected to be more reactive than the corresponding 2,4,6-tri-*t*-butylphenyl-substituted ones. Thus, we report here preparation of the 2,4-di-*t*-butyl-6-isopropylphenyl-substituted diphosphenes and some related species.

RESULTS AND DISCUSSION

Although a preparative method for 2-bromo-1,5-di-*t*-butyl-3-isopropylbenzene (1) by the bromination

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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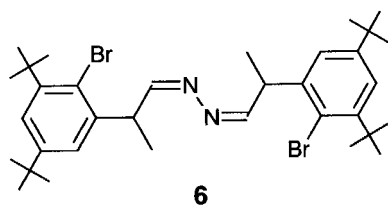
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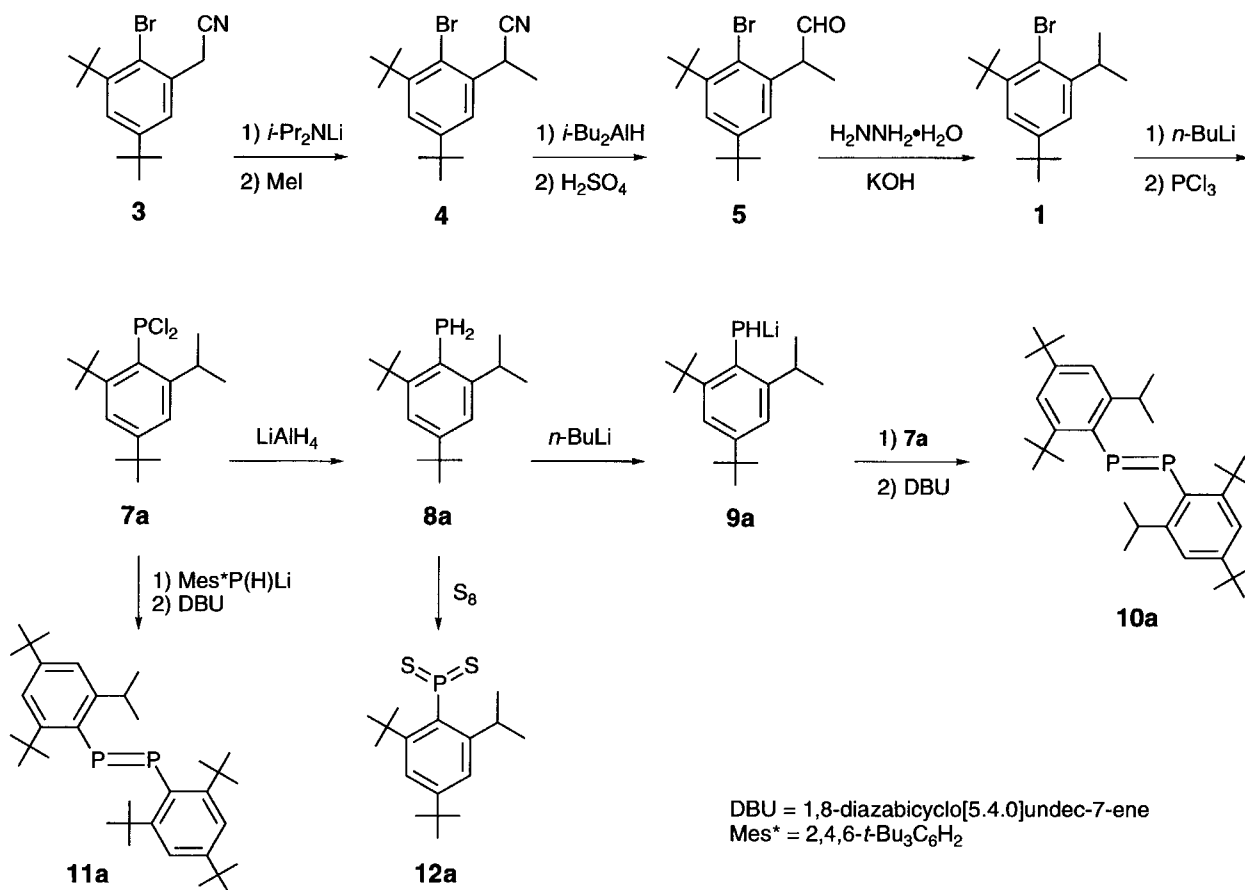
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reaction of 1,3-di-*t*-butyl-5-isopropylbenzene (**2**) was briefly reported in the literature [24] (no spectral data), the disadvantage of the laborious preparation of the starting **2** [24,25] prompted us to seek some other synthetic routes to **1** (Scheme 1). Thus, 2-bromo-1,5-di-*t*-butyl-3-(cyanomethyl)benzene (**3**) [23] was allowed to react successively with lithium diisopropylamide and iodomethane to give 2-bromo-1,5-di-*t*-butyl-3-(1-cyanoethyl)benzene (**4**, 95% yield), which was converted to the formyl derivative **5** (94% yield). The Wolff-Kishner reduction of **5** gave the desired **1** in 71% yield. In some cases, azine **6** was also obtained as a by-product. The compound **6** was also reduced, under the Wolff-Kishner conditions, to give **1** (74% yield).



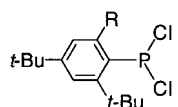
The substituted bromobenzene **1** was lithiated with

butyllithium in tetrahydrofuran (THF), and the resulting solution was allowed to react with phosphorus trichloride to give (2,4-di-*t*-butyl-6-isopropylphenyl)phosphonous dichloride (PxPCl₂, **7a**). Reduction of **7a** with lithium aluminum hydride gave (2,4-di-*t*-butyl-6-isopropylphenyl)phosphine (PxPH₂, **8a**). Tables 1 and 2 list ³¹P NMR data of **7a** and **8a**, respectively, and some related compounds. A ³¹P NMR signal due to **7a** appeared between those for DbtPCl₂ (**7b**) and Mes*PCl₂ (**7c**): The signal due to PxPCl₂ showed a downfield shift by ca. 11 ppm, compared with that of Mes*PCl₂, and an upfield shift by 3 ppm compared with that for DbtPCl₂. It is interesting to note that a signal due to Mes*PCl₂ appeared very close to that for MxPCl₂ (**7d**) containing an electron-donating dimethylamino group and in higher field than MoxPCl₂ (**7e**) bearing a methoxy group. Contrary to this, the ³¹P NMR chemical shift for PxPH₂ (**8a**) showed an upfield shift by 14 ppm, compared with that for Mes*PH₂, and very close to that for DbtPH₂ (difference in chemical shift: 0.9 ppm). In this case, the chemical shifts of Mes*PH₂ are very much different from those of Mx- or MoxPH₂.

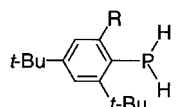


SCHEME 1

TABLE 1 ^{31}P NMR Data of Phosphonous Dichlorides **7** in CDCl_3

	Compound	R	$\delta_{\text{P}}^{\text{a}}$	Reference
	7a	<i>i</i> -Pr	164.5	this work
	7b	Me	167.5	[15]
	7c	<i>t</i> -Bu	153.8	[4,26]
	7d	NMe ₂	154.2	[17,26]
	7e	OMe	159.3	[20]

^aRelative to external 85% H_3PO_4 .**TABLE 2** ^{31}P NMR Data of Phosphines **8** in CDCl_3

	Compound	R	$\delta_{\text{P}}^{\text{a}}$	$^1\text{J}_{\text{PH}}$ (Hz)	Reference
	8a	<i>i</i> -Pr	-143.9	207.0	this work
	8b	Me	-143.0	203.0	[27,28]
	8c	<i>t</i> -Bu	-129.9	210.6	[15]
	8d	NMe ₂	-141.6	213.7	[17]
	8e	OMe	-155.4 ^b	207.4 ^b	[20]

^aRelative to external 85% H_3PO_4 .^bMeasured in C_6D_6 .

The phosphine PxPH_2 (**8a**) was metalated with butyllithium, and the resulting lithium phosphide [$\text{PxP}(\text{H})\text{Li}$, **9a**] was allowed to react successively with PxPCl_2 (**7a**) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give 1,2-bis(2,4-di-*t*-butyl-6-isopropylphenyl)diphosphene ($\text{PxP}=\text{PPx}$, **10a**) in 4% yield. Similarly, successive reactions of $\text{Mes}^*\text{P}(\text{H})\text{Li}$ with **7a** and DBU gave an unsymmetrical diphosphene $\text{PxP}=\text{PMes}^*$ (**11a**) in 18% yield. It should be noted that treatment of **7a** with *t*-butyllithium or lithium naphthalenide also formed the symmetrical diphosphene **10a**, although attempted separation of **10a** from by-products by using silica-gel or alumina column chromatography resulted in decomposition of **10a**. Table 3 shows ^{31}P NMR data of **10a**, **11a**, and some other diphosphenes. The ^{31}P NMR chemical shift for **10a** showed a downfield shift by ca. 18 ppm, compared with that for $\text{Mes}^*\text{P}=\text{PMes}^*$ (**10c**). A signal for $\text{MxP}=\text{PMx}$ appears at the field much higher than those for **10a,c**, probably because of the electron-donating effect of the dimethylamino group.

Reaction of PxPH_2 (**8a**) with elemental sulfur formed (2,4-di-*t*-butyl-6-isopropylphenyl)dithioxophosphorane [$\text{PxP}(=\text{S})_2$, **12a**]; however, **12a** was not isolated in pure form because of partial decomposition in the isolation process as well as difficulties in recrystallization. The ^{31}P NMR chemical shift of **12a** [δ_{P} (CDCl_3) 291.3] is close to that of $\text{DbtP}(=\text{S})_2$ [δ_{P} (CDCl_3) 289.4], while the signal due to $\text{Mes}^*\text{P}(=\text{S})_2$ showed a downfield shift [δ_{P} (CDCl_3) 298.2] compared with that for **12a**.

Thus, in the cases of phosphonous dichlorides and diphosphenes, a more bulky substituent (Mes^*) causes an upfield shift in the ^{31}P NMR, while the reverse tendency was observed in the cases of primary phosphines and dithioxophosphoranes. These results are apparently confusing. The electron-withdrawing effect of the chlorine atom bound to the sp^3 -phosphorus atom in RPCl_2 might be weakened by the bulky Mes^* group, due to distortion caused by steric repulsion. Similarly, the electronic-donating effect of the phosphorus-binding hydrogen atoms in Mes^*PH_2 may not be so effective as those of PxPH_2 and DbtPH_2 . In the case of $\text{DbtP}(=\text{S})_2$, the $-\text{P}(=\text{S})_2$ moiety is slightly deviated from planarity [30] and is less affected by the electron-withdrawing sulfur atoms, compared with the case of $\text{Mes}^*\text{P}(=\text{S})_2$, in which the $-\text{P}(=\text{S})_2$ moiety is planar [31]. In each case, the 2,4-di-*t*-butyl-6-isopropylphenyl-substituted derivatives showed their chemical shifts close to those of the corresponding 2,4-di-*t*-butyl-6-methylphenyl derivatives, indicating the unique character of the Mes^* group.

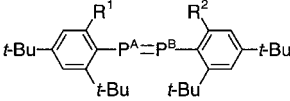
EXPERIMENTAL

Melting points were taken on a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^1H 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. Occasionally, ^1H 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 a JEOL HX-110 or a Hitachi M-2500S spectrometer.

2-Bromo-1,5-di-*t*-butyl-3-(1-cyanoethyl)benzene (**4**)

To a solution of 2-bromo-1,5-di-*t*-butyl-3-(cyano-methyl)benzene (**3**, 3.65 g, 11.9 mmol) [23] in THF (90 mL) was added 12.0 mmol of lithium diisopropylamide (2.0 M solution in heptane/tetrahydrofuran/ethylbenzene, 1 M = 1 mol dm^{-3}) at 0°C. The resulting mixture was treated with iodomethane (14.3 mmol), and the reaction mixture was stirred at room temperature for 1 day and extracted with ether. The organic phase was dried over MgSO_4 , and the solvent was removed under reduced pressure. Chromatographic treatment ($\text{SiO}_2/\text{benzene}$) of the residue afforded 3.64 g (95%) of **4**: colorless crystals, m.p. 117–118°C; ^1H NMR (200 MHz, CDCl_3) δ = 1.34

TABLE 3 ³¹P NMR Data of Diphosphenes **10** and **11** in C₆D₆

	Compound	R ¹	R ²	δ _P ^A	δ _P ^B	¹ J _{PP} /Hz	Reference
	10a	<i>i</i> -Pr	<i>i</i> -Pr	510.5			this work
	10c	<i>t</i> -Bu	<i>t</i> -Bu	492.4			[4]
	10d	NMe ₂	NMe ₂	428.2 ^b			[17]
	11a	<i>t</i> -Bu	<i>i</i> -Pr	484.9	515.1	582.2	this work
	11b	<i>t</i> -Bu	Me	480.1	517.0	583.5	[15]
	11d	<i>t</i> -Bu	NMe ₂	461.0	475.4	562.9	[29]
	11e	<i>t</i> -Bu	OMe	448.5 ^c	502.8 ^c	562.0 ^c	[20]

^aRelative to external 85% H₃PO₄.^bMeasured in C₆D₆/THF.^cMeasured in CDCl₃.

(9H, s, *t*-Bu), 1.54 (9H, s, *t*-Bu), 1.63 (3H, d, ³J_{HH} = 7.1 Hz, CHMe), 4.62 (1H, q, ³J_{HH} = 7.1 Hz, CHMe), 7.47 (1H, d, ⁴J_{HH} = 2.4 Hz, arom.), and 7.50 (1H, d, ⁴J_{HH} = 2.4 Hz, arom.); ¹³C[¹H] NMR (50 MHz, CDCl₃) δ = 20.5 (CHMe), 30.1 (CMe₃), 31.1 (CMe₃), 32.6 (CHMe), 34.9 (CMe₃), 37.6 (CMe₃), 120.1 (arom., CBr or CN), 121.9 (arom., CBr or CN), 123.2 (arom., CH), 125.3 (arom., CH), 137.7 (arom.), 148.4 (arom.), and 150.6 (arom.); IR (KBr) 2962, 2871, 2239, 1479, 1450, 1427, 1394, 1362, 1016, and 881 cm⁻¹; MS (70 eV) *m/z* (rel intensity) 323 (M⁺ + 2; 24), 321 (M⁺; 25), 308 (M⁺ - Me + 2; 99), and 306 (M⁺ - Me; 100). Found: *m/z* 321.1088. Calcd for C₁₇H₂₄BrN: M, 321.1092. Found: C, 63.07; H, 7.36; N, 4.28%. Calcd for C₁₇H₂₄BrN: C, 63.36; H, 7.51; N, 4.35%.

2-Bromo-1,5-di-*t*-butyl-3-(1-formylethyl)benzene (5)

To a solution of **4** (7.25 g, 22.5 mmol) in benzene (300 mL) was added 27.0 mmol of diisobutylaluminum hydride (1.01 M solution in toluene) at room temperature. The resulting mixture was stirred at ambient temperature for 4 hours. Then the reaction mixture was treated with H₂SO₄ and extracted with Et₂O. The organic phase was dried over MgSO₄, and the solvent was removed under reduced pressure to give 6.91 g (94%) of **5**: colorless crystals, m.p. 69–71°C; ¹H NMR (200 MHz, CDCl₃) δ = 1.30 (9H, s, *t*-Bu), 1.42 (3H, d, ³J_{HH} = 6.9 Hz, CHMe), 1.57 (9H, s, *t*-Bu), 4.38 (1H, q, ³J_{HH} = 6.9 Hz, CHMe), 6.92 (1H, d, ⁴J_{HH} = 2.3 Hz, arom.), 7.47 (1H, d, ⁴J_{HH} = 2.3 Hz, arom.), and 9.75 (1H, s, CHO); ¹³C[¹H] NMR (50 MHz, CDCl₃) δ = 14.5 (CHMe), 30.1 (CMe₃), 31.2 (CMe₃), 34.8 (CMe₃), 37.6 (CMe₃), 53.3 (CHMe), 122.7 (arom., CBr), 124.2 (arom., CH), 124.9 (arom., CH), 139.3 (arom.), 148.4 (arom.), 150.2 (arom.), and 201.1 (CHO); IR (KBr) 1726, 1458, 1396, 1365, and 1014 cm⁻¹; MS (70 eV) *m/z* (rel intensity) 326 (M⁺ + 2; 2), 324 (M⁺; 2), 295 (M⁺ - CHO; 15), 245

(M⁺ - Br; 23), and 57 (*t*-Bu⁺; 100). Found: *m/z* 324.1107. Calcd for C₁₇H₂₅BrO: M, 324.1089.

2-Bromo-1,5-di-*t*-butyl-3-isopropylbenzene (1)

A mixture of **5** (1.99 g, 6.12 mmol), hydrazine monohydrate (61.8 mmol), KOH (1.03 g, 18.4 mmol), triethylene glycol (75 mL), and water (7 mL) was heated at 130°C for 2 hours to remove water. Then the mixture was heated at 200°C for 6 hours. The resulting mixture was cooled to room temperature and worked up using ether and water. The organic phase was dried over MgSO₄, and the solvent was evaporated in vacuo. Chromatographic treatment (SiO₂/hexane-ether) of the residue afforded 1.35 g (71%) of **1**. In some cases, azine **6** was also obtained as a by-product (0–10% yields).

Compound **1**: Colorless crystals, m.p. 63–64°C (lit. [24] 69–70°C); ¹H NMR (200 MHz, CDCl₃) δ = 1.25 (6H, d, ³J_{HH} = 6.8 Hz, CHMe₂), 1.32 (9H, s, *t*-Bu), 1.56 (9H, s, *t*-Bu), 3.63 (1H, sept, ³J_{HH} = 6.8 Hz, CHMe₂), 7.18 (1H, d, ⁴J_{HH} = 2.5 Hz, arom.), and 7.36 (1H, d, ⁴J_{HH} = 2.5 Hz, arom.); ¹³C[¹H] NMR (50 MHz, CDCl₃) δ = 23.5 (CHMe₂), 30.5 (CMe₃), 31.5 (CMe₃), 33.6 (CHMe₂), 34.9 (CMe₃), 37.7 (CMe₃), 121.6 (arom., CH), 122.3 (arom., CBr), 123.2 (arom., CH), 147.3 (arom.), 148.3 (arom.), and 149.3 (arom.); UV (hexanes) 218 (sh, log ε 4.2), 234 (sh, 3.8), and 266 nm (sh, 2.8); IR (KBr) 1591, 1380, 1265, 1119, 1151, and 1072 cm⁻¹; MS (70 eV) *m/z* (rel intensity) 312 (M⁺ + 2; 14), 310 (M⁺; 11), 295 (M⁺ - Me; 36), 267 (M⁺ - *i*-Pr; 5), and 57 (*t*-Bu⁺; 100). Found: *m/z* 310.1266. Calcd for C₁₇H₂₇Br: M, 310.1296. Found: C, 65.38; H, 8.48%. Calcd for C₁₇H₂₇Br: C, 65.59; H, 8.74%.

Compound **6**: Colorless crystals, m.p. 150–152°C (decomp); ¹H NMR (200 MHz, CDCl₃) δ = 1.29 (18H, s, *t*-Bu), 1.45 (6H, d, ³J_{HH} = 6.9 Hz, CHMe), 1.56 (18H, s, *t*-Bu), 4.55 (2H, m, CHMe), 7.11 (2H, d, ⁴J_{HH} = 2.5 Hz, arom.), 7.40 (2H, d, ⁴J_{HH} = 2.5 Hz, arom.), and 7.92 (2H, d, ³J_{HH} = 4.3 Hz, CH=N); ¹³C[¹H]

NMR (50 MHz, CDCl_3) δ = 18.1 (CHMe), 30.3 (CMe_3), 31.3 (CMe_3), 34.8 (CMe_3), 37.6 (CHMe), 42.7 (CMe_3), 122.3 (arom., CBr), 123.6 (arom., CH), 124.2 (arom., CH), 142.2 (arom.), 147.9 (arom.), 149.7 (arom.), and 165.4 ($\text{C}=\text{N}$); UV (hexanes) 268 nm (log ϵ 3.09); IR (KBr) 2962, 2906, 2871, 1643, 1469, 1456, 1421, 1398, 1365, 1236, and 1014 cm^{-1} ; MS (70 eV) m/z (rel intensity) 648 ($\text{M}^+ + 4$; 2), 646 ($\text{M}^+ + 2$; 4), 644 (M^+ ; 2), 567 ($\text{M}^+ - \text{Br} + 2$; 100), 565 ($\text{M}^+ - \text{Br}$; 96), 351 ($\text{M}^+ - \text{C}_{16}\text{H}_{24}\text{Br} + 2$; 10), 349 ($\text{M}^+ - \text{C}_{16}\text{H}_{24}\text{Br}$; 9), 297 ($\text{C}_{16}\text{H}_{24}\text{Br}^+ + 2$; 11), and 295 ($\text{C}_{16}\text{H}_{24}\text{Br}^+$; 13). Found: m/z 644.2333. Calcd for $\text{C}_{34}\text{H}_{50}\text{Br}_2\text{N}_2$: M, 644.2341.

*(2,4-Di-*t*-butyl-6-isopropylphenyl)phosphonous Dichloride (7a)*

To a solution of **1** (508.2 mg, 1.63 mmol) in THF (17 mL) was added 1.80 mmol of butyllithium (1.54 M solution in hexane) at -78°C , and the reaction mixture was stirred for 30 minutes. The resulting solution was added dropwise to a THF (3 mL) solution of PCl_3 (4.90 mmol) at -78°C , and the reaction mixture was stirred for 1.5 hours at room temperature. Then the reaction mixture was treated with pentane and water, the organic phase was dried over MgSO_4 , and the solvent was evaporated to give 480 mg (88%) of **7a**: colorless needles, m.p. $128\text{--}131^\circ\text{C}$ (decomp); ^1H NMR (200 MHz, CDCl_3) δ = 1.32 (6H, d, $^3J_{\text{HH}} = 6.5$ Hz, CHMe), 1.33 (9H, s, *p*-*t*-Bu), 1.59 (9H, d, $^5J_{\text{PH}} = 1.4$ Hz, *o*-*t*-Bu), 4.35 (1H, d of sept, $^3J_{\text{HH}} = 6.5$ Hz and $^4J_{\text{PH}} = 1.0$ Hz, CHMe), 7.32 (1H, dd, $^4J_{\text{PH}} = 6.7$ Hz and $^4J_{\text{HH}} = 1.9$ Hz, arom.), and 7.36 (1H, d, $^4J_{\text{HH}} = 1.9$ Hz, arom.); $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3) δ = 24.8 (s, CHMe_2), 30.3 (d, $^3J_{\text{PC}} = 2.3$ Hz, CHMe_2), 31.0 (s, CMe_3), 34.1 (d, $^4J_{\text{PC}} = 23.9$ Hz, CMe_3), 35.3 (s, CMe_3), 37.4 (s, CMe_3), 120.8 (s, *m*-arom.), 124.3 (s, *m*-arom.), 132.6 (d, $^1J_{\text{PC}} = 83.9$ Hz, *ipso*-arom.), 154.0 (d, $^2J_{\text{PC}} = 36.8$ Hz, *o*-arom.), 154.9 (d, $^4J_{\text{PC}} = 0.8$ Hz, *p*-arom.), and 157.5 (d, $^2J_{\text{PC}} = 3.8$ Hz, *o*-arom.); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3) δ = 164.5; IR (KBr) 2964, 2931, 2908, 2870, 1597, 1363, and 480 cm^{-1} ; MS (70 eV) m/z (rel intensity) 336 ($\text{M}^+ + 4$; 3), 334 ($\text{M}^+ + 2$; 19), 332 (M^+ ; 28), 299 ($\text{M}^+ - \text{Cl} + 2$; 34), and 297 ($\text{M}^+ - \text{Cl}$; 100). Found: m/z 332.1209. Calcd for $\text{C}_{17}\text{H}_{27}\text{Cl}_2\text{P}$: M, 332.1227.

*(2,4-Di-*t*-butyl-6-isopropylphenyl)phosphine (8a)*

A mixture of **7a** (858.5 mg, 2.58 mmol), LiAlH_4 (2.78 mmol), and THF (40 mL) was stirred at 0°C for 15 minutes. Then the mixture was stirred at room temperature for 30 minutes, and the solvent was evaporated. Dry hexane (15 mL) was added to the residue

and insoluble material was removed by filtration under argon. Removal of the solvent under reduced pressure afforded crude **8a** (560 mg, ca. 82% yield): ^1H NMR (200 MHz, CDCl_3) δ = 1.28 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CHMe_2), 1.33 (9H, s, *t*-Bu), 1.56 (9H, s, *t*-Bu), 3.58 (1H, d of sept, $^3J_{\text{HH}} = 6.7$ Hz, $^4J_{\text{PH}} = 3.4$ Hz, CHMe_2), 4.03 (2H, d, $^1J_{\text{PH}} = 206.7$ Hz, PH_2), 7.23 (1H, m, arom.), and 7.39 (1H, dd, $^4J_{\text{HH}} = 2.2$ Hz, $^4J_{\text{PH}} = 3.1$ Hz, arom.); $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3) δ = 24.0 (s, CHMe_2), 31.4 (s, CMe_3), 32.0 (d, $^4J_{\text{PC}} = 9.1$ Hz, CMe_3), 32.5 (d, $^3J_{\text{PC}} = 9.5$ Hz, CHMe_2), 35.0 (s, CMe_3), 37.5 (s, CMe_3), 119.9 (d, $^3J_{\text{PC}} = 1.9$ Hz, *m*-arom.), 121.7 (d, $^3J_{\text{PC}} = 4.8$ Hz, *m*-arom.), 122.2 (d, $^1J_{\text{PC}} = 19.4$ Hz, *ipso*-arom.), 150.4 (s, *p*-arom.), 153.1 (d, $^2J_{\text{PC}} = 5.0$ Hz, *o*-arom.), and 153.5 (d, $^2J_{\text{PC}} = 12.0$ Hz, *o*-arom.); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3) δ = -143.9 (t, $^1J_{\text{PH}} = 207.0$ Hz); IR (KBr) 2960, 2868, 2376, 2287, 1599, 1462, and 1362 cm^{-1} ; MS (70 eV) m/z (rel intensity) 263 ($\text{M}^+ - 1$; 100), 249 ($\text{M}^+ - \text{Me}$; 18), 231 ($\text{M}^+ - \text{PH}_2$; 25), 217 ($\text{M}^+ - \text{PH}_2 - \text{Me} + 1$; 15), 208 ($\text{M}^+ - t\text{-Bu} + 1$; 13), 193 ($\text{M}^+ - t\text{-Bu} - \text{Me} + 1$; 22), 152 ($\text{M}^+ - 2t\text{-Bu} + 2$; 16), and 57 (*t*-Bu $^+$; 62).

*1,2-Bis(2,4-di-*t*-butyl-6-isopropylphenyl)diphosphene (10a)*

To a solution of crude **8a** (560 mg, 2.12 mmol) in THF (5 mL) was added 1.30 mmol of butyllithium (1.53 M solution in hexane) at -78°C , and the resulting mixture was warmed to ambient temperature and stirred for 1 hour. Then the mixture was added to a THF (5 mL) solution of **7a** (432.1 mg, 1.30 mmol) at 0°C , and the reaction mixture was stirred at room temperature for 30 minutes. To the mixture was added 1.43 mmol of DBU, and the resulting solution was stirred at 0°C for 1 hour. The solvent was removed in vacuo, and the residue was treated by column chromatography (SiO_2 /hexane-1% Et_3N) to give 28.2 mg (4% yield based on **7a**) of **10a**: yellow crystals, m.p. $143\text{--}145^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3) δ = 1.39 (12H, d, $^3J_{\text{HH}} = 6.7$ Hz, CHMe_2), 1.50 (18H, s, *t*-Bu), 1.64 (18H, s, *t*-Bu), 3.59 (2H, m, CHMe_2), 7.43 (2H, m, arom.), and 7.63 (2H, m, arom.); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3) δ = 506.9; UV (hexanes) 265 (log ϵ 4.16), 324 (3.70), and 467 nm (2.61); MS (70 eV) m/z (rel intensity) 524 (M^+ ; 53), 481 ($\text{M}^+ - i\text{-Pr}$; 4), 467 ($\text{M}^+ - t\text{-Bu}$; 12), 293 ($\text{M}^+ - \text{Px}$; 3), 263 ($\text{PxP}^+ + 1$; 100), and 231 (Px^+ ; 8). Found: m/z 524.3701. Calcd for $\text{C}_{34}\text{H}_{54}\text{P}_2$: M, 524.3701.

*1-(2,4-Di-*t*-butyl-6-isopropylphenyl)-2-(2,4,6-tri-*t*-butylphenyl)diphosphene (11a)*

To a solution of (2,4,6-tri-*t*-butylphenyl)phosphine (336.3 mg, 1.21 mmol) in THF (5 mL) was added

1.21 mmol of butyllithium (1.59 M solution in hexane) at -78°C , and the resulting mixture was warmed to ambient temperature and stirred for 30 minutes. Then the mixture was added to a THF (5 mL) solution of **7a** (402.7 mg, 1.21 mmol) at 0°C , and the reaction mixture was stirred at room temperature for 30 minutes. To the mixture was added 1.34 mmol of DBU, and the resulting solution was stirred for 2 hours. The solvent was removed under reduced pressure and the residue was treated by column chromatography ($\text{SiO}_2/\text{hexane}-0.5\%\text{Et}_3\text{N}$) to give 114.6 mg (18% yield) of **11a**: yellow crystals, m.p. $164\text{--}166^{\circ}\text{C}$; ^1H NMR (200 MHz, CDCl_3) δ = 1.29 (9H, s, *p*-*t*-Bu), 1.30 (6H, d, $^3J_{\text{HH}}$ = 6.6 Hz, CHMe_2), 1.30 (9H, s, *p*-*t*-Bu), 1.45 (9H, s, Px, *o*-*t*-Bu), 1.57 (18H, s, Mes*, *o*-*t*-Bu), 3.98 (1H, m, CHMe_2), 7.42 (1H, d, $^4J_{\text{HH}}$ = 2.0 Hz, *m*-Px), 7.57 (1H, m, *m'*-Px), and 7.62 (2H, s, *m*-Mes*); $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3) δ = 24.4 (s, CHMe_2), 31.3 (s, *p*- CMe_3), 31.4 (s, *p*- CMe_3), 32.6 (m, CHMe_2), 33.8 (m, *o*- CMe_3), 33.9 (m, *o*- CMe_3), 34.8 (s, CMe_3), 34.9 (s, CMe_3), 38.1 (s, CMe_3), 38.6 (s, CMe_3), 120.7 (s, *m*-Px), 122.0 (s, *m*-Px), 122.4 (s, *m*-Mes*), 136–139 (m, *ipso*-Px and *ipso*-Mes*), 149.4 (s, arom.), 150.9 (s, arom.), 152.7 (s, arom.), 153.8 (s, arom.), and 154.0 (s, arom.); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, C_6D_6) δ = 484.9 (Mes*P) and 515.1 (PxP), AB, $^1J_{\text{PP}}$ = 582.2 Hz; UV (hexanes) 278 (log ϵ 4.01), 329 (3.67), and 468 nm (2.59); IR (KBr) 2958, 2906, 2866, 1595, 1462, 1394, 1362, 1236, 876, and 499 cm^{-1} ; MS m/z (rel intensity) 538 (M^+ ; 11), 481 ($\text{M}^+ - t\text{-Bu}$; 48), 277 (Mes* $\text{P}^+ + 1$; 77), 263 (Px $\text{P}^+ + 1$; 100), and 220 (Px $\text{P}^+ - i\text{-Pr} + 1$; 24). Found: m/z 538.3856. Calcd for $\text{C}_{35}\text{H}_{56}\text{P}_2$: M, 538.3857.

(2,4-Di-*t*-butyl-6-isopropylphenyl)thioxophosphine Sulfide (**12a**)

A mixture of **8a** (307.3 mg, 1.16 mmol) and elemental sulfur (111.6 mg, 3.48 mg-atom) in toluene (10 mL) was heated under reflux for 9 hours. The ^{31}P NMR spectrum of the reaction mixture showed **12a** as a major product. Then the solvent was removed in vacuo. An attempt to obtain **12a** in pure form, by crystallization, failed due to its decomposition. **12a**: ^1H NMR (200 MHz, CDCl_3) δ = 1.42 (9H, s, *p*-*t*-Bu), 1.47 (6H, d, $^3J_{\text{HH}}$ = 6.5 Hz, CHMe_2), 1.79 (9H, s, *o*-*t*-Bu), 4.13 (1H, d of sept, $^3J_{\text{HH}}$ = 6.5 Hz and $^4J_{\text{PH}}$ = 4.5 Hz, CHMe_2), 7.26 (1H, m, arom.), and 7.54 (1H, dd, $^4J_{\text{PH}}$ = 7.7 Hz and $^4J_{\text{HH}}$ = 1.8 Hz, arom.); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3) δ = 291.3; MS (70 eV) m/z (rel intensity) 326 (M^+ ; 23), 293 ($\text{M}^+ - \text{S} - 1$; 100), 259 ($\text{M}^+ - 2\text{S} - 3$; 26), 217 ($\text{M}^+ - i\text{-Pr} - 2\text{S} - 2$; 10), and 57 (*t*-Bu $^+$; 16).

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