Heteroatom Chemistry
Volume 12, Number 5, 2001

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

Kozo Toyota, Yoshiaki Matsushita, Naoyuki Shinohara, and Masaaki Yoshifuji

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

Received 4 January 2001; revised 21 March 2001

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 phosphaquinones [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

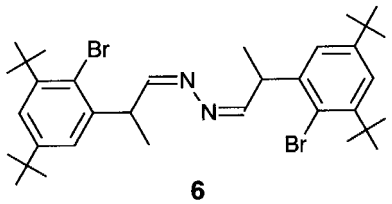
Although a preparative method for 2-bromo-1,5-di-*t*-butyl-3-isopropylbenzene (**1**) by the bromination

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

Correspondence to: Masaaki Yoshifuji.

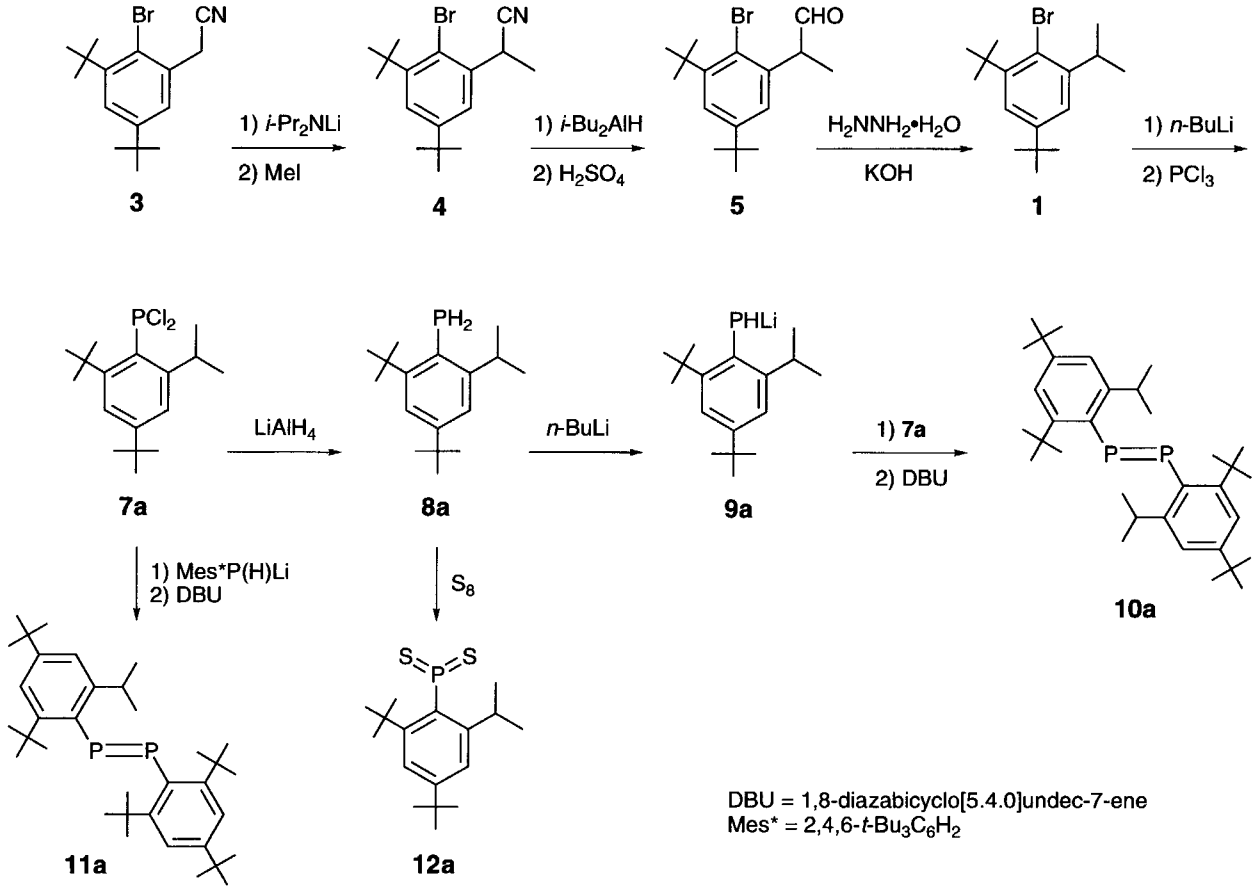
Contract Grant Sponsor: Ministry of Education, Science, Sports and Culture, Japan.
Contract Grant Number: Grant-in-Aid for Scientific Research on Priority Area No. 09239104.
Contract Grant Number: Grant-in-Aid for Scientific Research on Priority Area No. 12020205.

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).



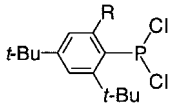
6

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 ($PxPCl_2$, **7a**). Reduction of **7a** with lithium aluminum hydride gave (2,4-di-*t*-butyl-6-isopropylphenyl)phosphine ($PxPH_2$, **8a**). Tables 1 and 2 list ^{31}P NMR data of **7a** and **8a**, respectively, and some related compounds. A ^{31}P NMR signal due to **7a** appeared between those for $DbtPCl_2$ (**7b**) and Mes^*PCl_2 (**7c**): The signal due to $PxPCl_2$ showed a downfield shift by ca. 11 ppm, compared with that of Mes^*PCl_2, and an upfield shift by 3 ppm compared with that for $DbtPCl_2$. It is interesting to note that a signal due to Mes^*PCl_2 appeared very close to that for $MxPCl_2$ (**7d**) containing an electron-donating dimethylamino group and in higher field than $MoxPCl_2$ (**7e**) bearing a methoxy group. Contrary to this, the ^{31}P NMR chemical shift for $PxPH_2$ (**8a**) showed an upfield shift by 14 ppm, compared with that for Mes^*PH_2, and very close to that for $DbtPH_2$ (difference in chemical shift: 0.9 ppm). In this case, the chemical shifts of Mes^*PH_2 are very much different from those of Mx- or $MoxPH_2$.



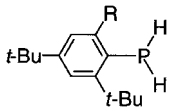
SCHEME 1

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

	Compound	R	δ_P[a]	Reference
	**7a**	*i*-Pr	164.5	this work
	7b	Me	167.5	[15]
	7c	*t*-Bu	153.8	[4,26]
	7d	NMe_2	154.2	[17,26]
	7e	OMe	159.3	[20]

[a]Relative to external 85% H_3PO_4.

TABLE 2 ^{31}P NMR Data of Phosphines **8** in $CDCl_3$

	Compound	R	δ_P[a]	$^1J_{PH}$ (Hz)	Reference
	**8a**	*i*-Pr	−143.9	207.0	this work
	8b	Me	−143.0	203.0	[27,28]
	8c	*t*-Bu	−129.9	210.6	[15]
	8d	NMe_2	−141.6	213.7	[17]
	8e	OMe	−155.4[b]	207.4[b]	[20]

[a]Relative to external 85% H_3PO_4.
[b]Measured in C_6D_6.

The phosphine $PxPH_2$ (**8a**) was metalated with butyllithium, and the resulting lithium phosphide [PxP(H)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 (PxP=PPx, **10a**) in 4% yield. Similarly, successive reactions of Mes*P(H)Li with **7a** and DBU gave an unsymmetrical diphosphene PxP=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 Mes*P=PMes* (**10c**). A signal for MxP=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 [$PxP(=S)_2$, **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 $DbtP(=S)_2$ [δ_p ($CDCl_3$) 289.4], while the signal due to $Mes^*P(=S)_2$ 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 $DbtP(=S)_2$, the $-P(=S)_2$ moiety is slightly deviated from planarity [30] and is less affected by the electron-withdrawing sulfur atoms, compared with the case of $Mes^*P(=S)_2$, in which the $-P(=S)_2$ 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.

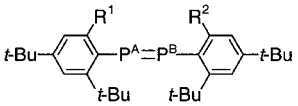
EXPERIMENTAL

Melting points were taken on a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^{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. Occasionally, ^{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 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-(cyanomethyl)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 (SiO_2/benzene) of the residue afforded 3.64 g (95%) of **4**: colorless crystals, m.p. 117–118°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.34

TABLE 3 ^{31}P NMR Data of Diphosphenes **10** and **11** in C_6D_6



Compound	R^1	R^2	δ_PA[a]	δ_PB[a]	$^1J_{PP}$/Hz	Reference
10a	*i*-Pr	*i*-Pr	510.5			this work
10c	*t*-Bu	*t*-Bu	492.4			[4]
10d	NMe_2	NMe_2	428.2[b]			[17]
11a	*t*-Bu	*i*-Pr	484.9	515.1	582.2	this work
11b	*t*-Bu	Me	480.1	517.0	583.5	[15]
11d	*t*-Bu	NMe_2	461.0	475.4	562.9	[29]
11e	*t*-Bu	OMe	448.5[c]	502.8[c]	562.0[c]	[20]

[a]Relative to external 85% H_3PO_4.
[b]Measured in C_6D_6/THF.
[c]Measured in $CDCl_3$.

(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.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 20.5 (CHMe), 30.1 (CMe_3), 31.1 (CMe_3), 32.6 (CHMe), 34.9 (CMe_3), 37.6 (CMe_3), 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 $C_{17}H_{24}BrN$: M, 321.1092. Found: C, 63.07; H, 7.36; N, 4.28%. Calcd for $C_{17}H_{24}BrN$: 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 H_2SO_4 and extracted with Et_2O. The organic phase was dried over $MgSO_4$, 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, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 14.5 (CHMe), 30.1 (CMe_3), 31.2 (CMe_3), 34.8 (CMe_3), 37.6 (CMe_3), 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 $C_{17}H_{25}BrO$: 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 $MgSO_4$, and the solvent was evaporated in vacuo. Chromatographic treatment (SiO_2/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, $CDCl_3$) δ = 1.25 (6H, d, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 1.32 (9H, s, *t*-Bu), 1.56 (9H, s, *t*-Bu), 3.63 (1H, sept, $^3J_{HH}$ = 6.8 Hz, CHMe_2), 7.18 (1H, d, $^4J_{HH}$ = 2.5 Hz, arom.), and 7.36 (1H, d, $^4J_{HH}$ = 2.5 Hz, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 23.5 (CHMe_2), 30.5 (CMe_3), 31.5 (CMe_3), 33.6 (CHMe_2), 34.9 (CMe_3), 37.7 (CMe_3), 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 $C_{17}H_{27}Br$: M, 310.1296. Found: C, 65.38; H, 8.48%. Calcd for $C_{17}H_{27}Br$: C, 65.59; H, 8.74%.

Compound **6**: Colorless crystals, m.p. 150–152°C (decomp); ^1H NMR (200 MHz, $CDCl_3$) 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); $^{13}C\{^1H\}$

NMR (50 MHz, $CDCl_3$) δ = 18.1 (CHMe), 30.3 ($C\underline{Me}_3$), 31.3 ($C\underline{Me}_3$), 34.8 ($\underline{C}Me_3$), 37.6 ($\underline{C}HMe$), 42.7 ($\underline{C}Me_3$), 122.3 (arom., CBr), 123.6 (arom., CH), 124.2 (arom., CH), 142.2 (arom.), 147.9 (arom.), 149.7 (arom.), and 165.4 (C=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 (M^+ + 4; 2), 646 (M^+ + 2; 4), 644 (M^+; 2), 567 (M^+ − Br + 2; 100), 565 (M^+ − Br; 96), 351 (M^+ − $C_{16}H_{24}Br$ + 2; 10), 349 (M^+ − $C_{16}H_{24}Br$; 9), 297 ($C_{16}H_{24}Br^+$ + 2; 11), and 295 ($C_{16}H_{24}Br^+$; 13). Found: *m/z* 644.2333. Calcd for $C_{34}H_{50}Br_2N_2$: 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. 128–131°C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.32 (6H, d, $^3J_{HH}$ = 6.5 Hz, CH$\underline{Me}$), 1.33 (9H, s, *p-t*-Bu), 1.59 (9H, d, $^5J_{PH}$ = 1.4 Hz, *o-t*-Bu), 4.35 (1H, d of sept, $^3J_{HH}$ = 6.5 Hz and $^4J_{PH}$ = 1.0 Hz, C$\underline{H}$Me), 7.32 (1H, dd, $^4J_{PH}$ = 6.7 Hz and $^4J_{HH}$ = 1.9 Hz, arom.), and 7.36 (1H, d, $^4J_{HH}$ = 1.9 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 24.8 (s, CH$\underline{Me}_2$), 30.3 (d, $^3J_{PC}$ = 2.3 Hz, $\underline{C}HMe_2$), 31.0 (s, C$\underline{Me}_3$), 34.1 (d, $^4J_{PC}$ = 23.9 Hz, C$\underline{Me}_3$), 35.3 (s, C$\underline{Me}_3$), 37.4 (s, C$\underline{Me}_3$), 120.8 (s, *m*-arom.), 124.3 (s, *m*-arom.), 132.6 (d, $^1J_{PC}$ = 83.9 Hz, *ipso*-arom.), 154.0 (d, $^2J_{PC}$ = 36.8 Hz, *o*-arom.), 154.9 (d, $^4J_{PC}$ = 0.8 Hz, *p*-arom.), and 157.5 (d, $^2J_{PC}$ = 3.8 Hz, *o*-arom.); ^{31}P{^{1}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 (M^+ + 4; 3), 334 (M^+ + 2; 19), 332 (M^+; 28), 299 (M^+ − Cl + 2; 34), and 297 (M^+ − Cl; 100). Found: *m/z* 332.1209. Calcd for $C_{17}H_{27}Cl_2P$: 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): ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.28 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH$\underline{Me}_2$), 1.33 (9H, s, *t*-Bu), 1.56 (9H, s, *t*-Bu), 3.58 (1H, d of sept, $^3J_{HH}$ = 6.7 Hz, $^4J_{PH}$ = 3.4 Hz, C$\underline{H}Me_2$), 4.03 (2H, d, $^1J_{PH}$ = 206.7 Hz, PH_2), 7.23 (1H, m, arom.), and 7.39 (1H, dd, $^4J_{HH}$ = 2.2 Hz, $^4J_{PH}$ = 3.1 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 24.0 (s, CH$\underline{Me}_2$), 31.4 (s, C$\underline{Me}_3$), 32.0 (d, $^4J_{PC}$ = 9.1 Hz, C$\underline{Me}_3$), 32.5 (d, $^3J_{PC}$ = 9.5 Hz, $\underline{C}HMe_2$), 35.0 (s, C$\underline{Me}_3$), 37.5 (s, C$\underline{Me}_3$), 119.9 (d, $^3J_{PC}$ = 1.9 Hz, *m*-arom.), 121.7 (d, $^3J_{PC}$ = 4.8 Hz, *m*-arom.), 122.2 (d, $^1J_{PC}$ = 19.4 Hz, *ipso*-arom.), 150.4 (s, *p*-arom.), 153.1 (d, $^2J_{PC}$ = 5.0 Hz, *o*-arom.), and 153.5 (d, $^2J_{PC}$ = 12.0 Hz, *o*-arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = −143.9 (t, $^1J_{PH}$ = 207.0 Hz); IR (KBr) 2960, 2868, 2376, 2287, 1599, 1462, and 1362 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 263 (M^+ − 1; 100), 249 (M^+ − Me; 18), 231 (M^+ − PH_2; 25), 217 (M^+ − PH_2 − Me + 1; 15), 208 (M^+ − *t*-Bu + 1; 13), 193 (M^+ − *t*-Bu − Me + 1; 22), 152 (M^+ − 2*t*-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. 143–145°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.39 (12H, d, $^3J_{HH}$ = 6.7 Hz, CH$\underline{Me}_2$), 1.50 (18H, s, *t*-Bu), 1.64 (18H, s, *t*-Bu), 3.59 (2H, m, C$\underline{H}Me_2$), 7.43 (2H, m, arom.), and 7.63 (2H, m, arom.); ^{31}P{^{1}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 (M^+ − *i*-Pr; 4), 467 (M^+ − *t*-Bu; 12), 293 (M^+ − Px; 3), 263 (PxP^+ + 1; 100), and 231 (Px^+; 8). Found: *m/z* 524.3701. Calcd for $C_{34}H_{54}P_2$: 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 (SiO_2/hexane-0.5%Et_3N) to give 114.6 mg (18% yield) of **11a**: yellow crystals, m.p. 164–166°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.29 (9H, s, *p*-*t*-Bu), 1.30 (6H, d, $^3J_{HH}$ = 6.6 Hz, CH$\underline{Me}_2$), 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, C$\underline{H}Me_2$), 7.42 (1H, d, $^4J_{HH}$ = 2.0 Hz, *m*-Px), 7.57 (1H, m, *m′*-Px), and 7.62 (2H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 24.4 (s, CH$\underline{Me}_2$), 31.3 (s, *p*-C$\underline{Me}_3$), 31.4 (s, *p*-C$\underline{Me}_3$), 32.6 (m, $\underline{C}HMe_2$), 33.8 (m, *o*-C$\underline{Me}_3$), 33.9 (m, *o*-C$\underline{Me}_3$), 34.8 (s, $\underline{C}Me_3$), 34.9 (s, $\underline{C}Me_3$), 38.1 (s, $\underline{C}Me_3$), 38.6 (s, $\underline{C}Me_3$), 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}P{^{1}H} NMR (81 MHz, C_6D_6) δ = 484.9 (Mes*P) and 515.1 (PxP), AB, $^1J_{PP}$ = 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 ($M^+ - t$-Bu; 48), 277 (Mes*P^+ + 1; 77), 263 (PxP^+ + 1; 100), and 220 (Px$P^+ - i$-Pr + 1; 24). Found: *m/z* 538.3856. Calcd for $C_{35}H_{56}P_2$: 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**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.42 (9H, s, *p*-*t*-Bu), 1.47 (6H, d, $^3J_{HH}$ = 6.5 Hz, CH$\underline{Me}_2$), 1.79 (9H, s, *o*-*t*-Bu), 4.13 (1H, d of sept, $^3J_{HH}$ = 6.5 Hz and $^4J_{PH}$ = 4.5 Hz, C$\underline{H}Me_2$), 7.26 (1H, m, arom.), and 7.54 (1H, dd, $^4J_{PH}$ = 7.7 Hz and $^4J_{HH}$ = 1.8 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 291.3; MS (70 eV) *m/z* (rel intensity) 326 (M^+; 23), 293 (M^+ − S − 1; 100), 259 (M^+ − 2S − 3; 26), 217 ($M^+ - i$-Pr − 2S − 2; 10), and 57 (*t*-Bu^+; 16).

REFERENCES

[1] Regitz, M.; Scherer, O. J., Eds. Multiple Bonds and Low Coordination in Phosphorus Chemistry; Georg Thieme Verlag: Stuttgart, Germany, 1990.
[2] Norman, N. C. Polyhedron 1993, 12, 2431.
[3] Dillon, K. B.; Mathey, F.; Nixon, J. F. Phosphorus: The Carbon Copy; John Wiley and Sons: Chichester, U.K., 1998.
[4] (a) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. J Am Chem Soc 1981, 103, 4587; (b) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. J Am Chem Soc 1982, 104, 6167.
[5] Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. Tetrahedron Lett 1984, 25, 1809.
[6] Yoshifuji, M.; Toyota, K.; Inamoto, N. J Chem Soc Chem Commun 1984, 689.
[7] Yoshifuji, M.; Sasaki, S.; Inamoto, N. J Chem Soc Chem Commun 1989, 1732.
[8] Karsch, H. H.; Köhler, F. H.; Reisacher, H.-U. Tetrahedron Lett 1984, 25, 3687.
[9] Appel, R.; Fölling, P.; Josten, B.; Siray, M.; Winkhaus, V.; Knoch, F. Angew Chem Int Ed Engl 1984, 23, 619.
[10] Ramdane, H.; Ranaivonjatovo, H.; Escudié, J.; Mathieu, S.; Knouzi, N. Organometallics 1996, 15, 3070.
[11] Rigon, L.; Ranaivonjatovo, H.; Escudié, J.; Dubourg, A.; Declercq, J.-P. Chem Eur J 1999, 5, 774.
[12] Toyota, K.; Tashiro, K.; Yoshifuji, M. Angew Chem Int Ed Engl 1993, 32, 1163.
[13] Märkl, G.; Hennig, R.; Raab, K. M. Chem Commun 1996, 2057.
[14] Sasaki, S.; Murakami, F.; Yoshifuji, M. Angew Chem Int Ed Engl 1999, 38, 340.
[15] Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Matsushita, T.; Nishimoto, K. J Am Chem Soc 1983, 105, 2495.
[16] Yoshifuji, M.; Ito, S.; Toyota, K.; Yasunami, M. Heteroat Chem 1996, 7, 23.
[17] Yoshifuji, M.; Hirano, M.; Toyota, K. Tetrahedron Lett 1993, 34, 1043.
[18] Yoshifuji, M.; Sangu, S.; Hirano, M.; Toyota, K. Chem Lett 1993, 1715.
[19] Yoshifuji, M.; Sangu, S.; Kamijo, K.; Toyota, K. Chem Ber 1996, 129, 1049.
[20] Yoshifuji, M.; An, D.-L.; Toyota, K.; Yasunami, M. Chem Lett 1993, 2069.
[21] Yoshifuji, M.; An, D.-L.; Toyota, K.; Yasunami, M. Tetrahedron Lett 1994, 35, 4379.
[22] Yoshifuji, M.; Higeta, N.; An, D.-L.; Toyota, K. Chem Lett 1998, 17.
[23] Yoshifuji, M.; Kamijo, K.; Toyota, K. Chem Lett 1994, 1931.
[24] Akkerman, O. S. Recl Trav Chim Pays-Bas 1967, 86, 1018.
[25] Scharf, H.-D.; Döring, F. Chem Ber 1967, 100, 1761.
[26] Yoshifuji, M.; Kamijo, K.; Toyota, K. Bull Chem Soc Jpn 1993, 3440, 66.
[27] Baudler, M.; Simon, J. Chem Ber 1988, 121, 281.
[28] Kamijo, K.; Otoguro, A.; Toyota, K.; Yoshifuji, M. Bull Chem Soc Jpn 1999, 72, 1335.
[29] Yoshifuji, M.; Hirano, M.; Sangu, S.; Toyota, K. Science Report Tohoku Univ Ser I 1992, 75, 1.
[30] Beckmann, H.; Großmann, G.; Ohms, G.; Sieler, Heteroat Chem 1994, 5, 73.
[31] Appel, R.; Knoch, F.; Kunze, H. Angew Chem Int Ed Engl 1983, 22, 1004.