

Reactions of tris(2,6-dimethoxyphenyl) arsine, tris(2,6-dimethoxyphenyl) stibine and tris(2,6-dimethoxyphenyl) bismuthine and their derivatives

Masanori Wada^{*}, Shin-ichi Miyake, Shinji Hayashi, Hiroshi Ohba, Shin-ichi Nobuki, Shuichi Hayase, Tatsuo Erabi

Department of Materials Science, Faculty of Engineering, Tottori University, Koyama, Tottori 680, Japan

Received 1 February 1995; in revised form 11 May 1995

Abstract

Tris(2,6-dimethoxyphenyl)arsine and tris(2,6-dimethoxyphenyl)stibine (Φ_3M ($\Phi = 2,6-(\text{MeO})_2\text{C}_6\text{H}_3$; $M = \text{As}$ or Sb)) reacted with common alkyl halides (RX) to give $[\Phi_3M-R]X$, while $\Phi_3\text{Bi}$ was unreactive in benzene, or it decomposed in hot alcohols. The reactions of Φ_3M (As,Sb) with butyl bromide in acetonitrile were much faster than that of triphenylphosphine. Treatments of Φ_3M (P,As,Sb) with *N*-bromosuccinimide (NBS) gave $[\Phi_3M-OH]Br$, while $\Phi_3\text{Bi}$ decomposed to give 1-bromo-2,6-dimethoxybenzene. $[\Phi_3M-OH]Br$ are soluble in water, and the acidity decreased in the order $M = \text{P} > \text{As} > \text{Sb}$. Treatments of Φ_3M (As,Sb) with aqueous hydrogen peroxide gave the oxides as hydrates, $\Phi_3MO \cdot x\text{H}_2\text{O}$ ($x = 1$ for $M = \text{As}$ and $x = 3$ for $M = \text{Sb}$), while $\Phi_3\text{Bi}$ was unreactive or decomposed. $\Phi_3\text{PO}$ was brominated by NBS to give $\Phi'_3\text{PO} \cdot \text{H}_2\text{O}$ ($\Phi' = 3\text{-Br-2,6-(MeO)}_2\text{C}_6\text{H}_2$), which did not react with perchloric acid. In contrast, $\Phi_3MO \cdot x\text{H}_2\text{O}$ (P,As,Sb) reacted with the acid to form the stable hydroxyonium salts $[\Phi_3M-OH]ClO_4$. $[\Phi_3P-OH]ClO_4$ formed crystals of stable 1:1 adducts with a variety of amines. $[\Phi_3As-OH]ClO_4$ formed 1:1 adducts when treated with excess amounts of several amines (triethylamine, diethylamine, isobutylamine and piperidine), but they were unstable to leave amines by recrystallization. $[\Phi_3Sb-OH]ClO_4$ formed unstable adducts with these amines, or it did not form. $[\Phi_3P-SH]ClO_4$ formed 1:1 adducts with several amines, or it was deprotonated to give $\Phi_3\text{PS}$. $\Phi_3MO \cdot x\text{H}_2\text{O}$ (P,As) reacted with common RX ($X = \text{Br}$ or I) to give $[\Phi_3M-OR]X$, but $\Phi_3\text{SbO} \cdot 3\text{H}_2\text{O}$ reacted to give $[\Phi_3Sb-OH]X$. $[\Phi_3P-OR]X$ decomposed reversibly to give $\Phi_3\text{PO}$ in solutions, although $[\Phi_3M-OR]ClO_4$ (P,As) could be recrystallized.

Keywords: Arsenic; Antimony; Bismuth; Phosphorus; Alkoxide; Amine

1. Introduction

As part of our systematic investigation on the chemistry of 2,6-dimethoxyphenyl derivatives such as tris(2,6-dimethoxyphenyl)phosphine ($\Phi_3\text{P}$ ($\Phi = 2,6-(\text{MeO})_2\text{C}_6\text{H}_3$)) [1–3], we attempted to work on a series of its derivatives of group 15 elements. Tris(2,6-dimethoxyphenyl)arsine, tris(2,6-dimethoxyphenyl)stibine and tris(2,6-dimethoxyphenyl)bismuthine, (Φ_3M ($M = \text{As}$, Sb and Bi respectively)) have been prepared by Horner and Simons [4], but their chemical properties have not been explored. The reactions reported here are summarized in Schemes 1 and 2. Some of the preliminary results have been reported elsewhere [5,6].

2. Experimental details

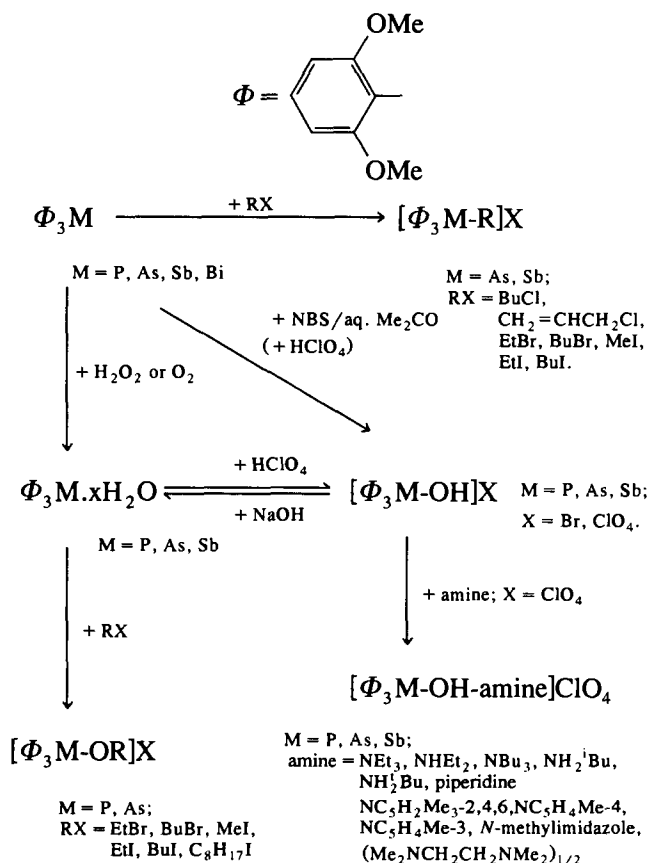
2.1. Physical measurements

^1H and ^{13}C NMR spectra were recorded for solutions in CDCl_3 or in CD_2Cl_2 using a JEOL model JNM-GX-270 spectrometer, and the representative ^1H and ^{13}C NMR spectral data are summarized in Tables 1 and 2 respectively. IR spectra (Nujol mulls) were recorded using a Shimadzu FTIR-4200 spectrophotometer.

2.2. Preparation of starting materials

$\Phi_3\text{P}$ was prepared as described elsewhere [1], or it was kindly provided by K.I. Kasei Co., Ltd. $\Phi_3\text{PO}$ [2], $\Phi_3\text{PS}$ [7] and $[\Phi_3P-SH]ClO_4$ [7] were prepared as previously reported.

^{*} Corresponding author.

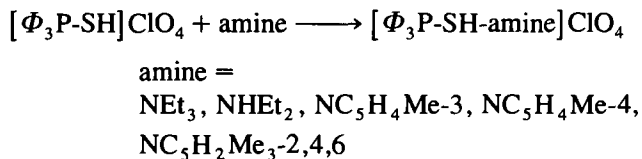


Scheme 1. Reactions of Φ_3M ($M = P, As, Sb$ or Bi) and their derivatives.

Φ_3As , Φ_3Sb and Φ_3Bi were prepared by analogous methods reported by Horner and Simons [4] with slight modification, as described below.

2.2.1. Φ_3As

The organolithium reagent ΦLi was prepared from 1,3-dimethoxybenzene (5.2 ml, 40 mmol), 15% *n*-hexane solution of *n*-butyllithium (25 ml, 40 mmol) and *N,N,N',N'*-tetramethylethylenediamine (about 0.1 ml) in dry diethyl ether (30 ml). The reagents were mixed at 0°C under argon, and the mixture was stirred at room temperature for 2 h to give a white suspension of ΦLi . Arsine trichloride (1.0 ml, 12 mmol) was added at 0°C, and the mixture was stirred at room temperature overnight. Methanol (20 ml) was added, and the mixture was concentrated to about a half volume under reduced pressure. The resultant white precipitates were filtered in air and were recrystallized from methanol to give



Scheme 2. Reactions of $[\Phi_3M-SH]ClO_4$ and amines.

white crystals of Φ_3As with a 78% yield (melting point (m.p.), 162–164°C (160°C [4])). Anal. Found: C, 59.38; H, 5.76. $C_{24}H_{27}AsO_6$ calc.: C, 59.27; H, 5.59%.

2.2.2. Φ_3Sb

In an analogous manner to the above using stibine trichloride (3.42 g, 15 mmol), Φ_3Sb was obtained as white crystals with a 82% yield (m.p., 165–167°C (after recrystallization from methanol) (163°C [4])). Anal. Found: C, 53.83; H 5.36. $C_{24}H_{27}SbO_6$ calc.: C, 54.06; H, 5.10%.

2.2.3. Φ_3Bi

To a suspension of ΦLi , prepared as above, was added an ethereal solution (30 ml) of bismuth trichloride (4.73 g, 15 mmol) at 0°C under argon, and the mixture was worked up as above. The resultant precipitates were dissolved in acetone to remove inorganic impurities by filtration. To the filtrate was added water to give precipitates of Φ_3Bi with a 78% yield. The analytical sample was obtained by recrystallization from 2-propanol with minimum heating (m.p., 155–157°C (128°C [4])). Anal. Found: C, 46.48; H, 4.54. $C_{24}H_{27}BiO_6$ calc.: C, 46.64; H, 4.39%.

2.2.4. Air oxidations of Φ_3M

Each solution of Φ_3M ($M = P, As$ or Sb) (0.3 mmol) in 2-propanol (15 ml) was heated at 80°C in air for 12 h, the solvent was removed under reduced pressure, and the residue was served for measurement of 1H NMR spectra to show the relative $\Phi_3M : \Phi_3MO \cdot xH_2O$ ratios as 8 : 92 ($M = P$), 17 : 83 ($M = As$) and 14 : 86 ($M = Sb$).

When Φ_3Bi was heated in an analogous manner, it decomposed to give 1,3-dimethoxybenzene.

2.3. Reactions of Φ_3M with alkyl halides

2.3.1. Reactions with alkyl iodides

A mixture of Φ_3Sb (0.533 g, 1 mmol) and butyl iodide (0.3 ml) in benzene (10 ml) was stirred at room temperature for several hours to give precipitates of $[\Phi_3Sb-Bu]I$ with a 78% yield. The analytical sample was obtained by recrystallization from 2-propanol (m.p., 171–173°C). Anal. Found: C, 46.55; H, 5.09. $C_{28}H_{36}IO_6Sb$ calc.: C, 46.89; H, 5.04%.

In analogous manners to the above, the following compounds were obtained.

$[\Phi_3As-Me]I$: 95% yield; m.p., not observed below 235°C. Anal. Found: C, 47.59; H, 4.86. $C_{25}H_{30}AsIO_6$ calc.: C, 47.79; H, 4.81%.

$[\Phi_3As-Et]I$: 99% yield; m.p., 235°C (decomposed). Anal. Found: C, 48.55; H, 5.12. $C_{26}H_{32}AsIO_6$ calc.: C, 48.62; H, 5.02%.

$[\Phi_3As-Bu]I$: 93% yield; m.p., 207°C (decomposed). Anal. Found: C, 50.20; H, 5.57. $C_{28}H_{36}AsIO_6$ calc.: C, 50.16; H, 5.41%.

[$\Phi_3\text{Sb-Me}$]I: 96% yield; m.p. 214°C (decomposed)
Anal. Found: C, 44.36; H, 4.52. $\text{C}_{25}\text{H}_{30}\text{IO}_6\text{Sb}$ calc.: C, 44.47; H, 4.58%.

[$\Phi_3\text{Sb-Et}$]I: 94% yield; m.p., 205–207°C. Anal. Found: C, 45.15; H, 4.76. $\text{C}_{26}\text{H}_{32}\text{IO}_6\text{Sb}$ calc.: C, 45.31; H, 4.68%.

$\Phi_3\text{Bi}$ was recovered with a 86% yield after heating in benzene containing ethyl iodide in a sealed glass tube for 15 h at 80°C.

2.3.2. Reactions with alkyl bromides

A mixture of $\Phi_3\text{Sb}$ (0.533 g, 1 mmol) and butyl bromide (0.6 ml) in methanol (10 ml) was heated at

80°C in a sealed glass tube for 15 h. Volatile materials were removed under reduced pressure, and the residue was washed with benzene to give [$\Phi_3\text{Sb-Bu}$]Br with a 86% yield (m.p., 142°C (decomposed)).

In analogous manners to the above, the following compounds were obtained.

[$\Phi_3\text{As-Et}$]Br: 98% yield; m.p., 237°C (decomposed).

[$\Phi_3\text{As-Bu}$]Br: 99% yield; m.p., 201°C (decomposed).

[$\Phi_3\text{As-Et}$]Br: 92% yield; m.p., 184°C (decomposed).

These compounds were characterized by ^1H NMR

Table 1
 ^1H NMR spectral data for some 2,6-dimethoxyphenyl derivatives ^a

Compounds	δ (ppm) [J_p (Hz)]			
	4-H ^b	3,5-H ^c	2,6-MeO ^d	Others
$\Phi_3\text{As}$	7.12	6.44	3.47	
$\Phi_3\text{Sb}$	7.13	6.44	3.47	
$\Phi_3\text{Bi}$	7.11	6.59	3.45	
$\Phi_3\text{AsO.H}_2\text{O}$	7.30	6.52	3.55	
$\Phi_3\text{SbO.3H}_2\text{O}$	7.35	6.63	3.71	
[$\Phi_3\text{P-OH}$]Br	7.48	6.58	3.61	
[$\Phi_3\text{P-OH}$]ClO ₄	7.51	6.61	3.65	
[$\Phi_3\text{As-OH}$]X (X = Br or ClO ₄)	7.57	6.71	3.72	
[$\Phi_3\text{Sb-OH}$]X (X = Br or ClO ₄)	7.58	6.74	3.76	
$\Phi_3'\text{PO.H}_2\text{O}$	7.52 ^e	6.49	3.85 and 3.38	
[$\Phi_3\text{P-OH-NEt}_3$]ClO ₄	7.31	6.51	3.50	3.01q[7], 1.22t[7]
[$\Phi_3\text{As-OH-NEt}_3$]ClO ₄	7.42	6.61	3.58	2.72q[7], 1.12t[7]
[$\Phi_3\text{P-SH-NEt}_3$]ClO ₄	7.25	6.50	3.53	3.16q[7], 1.33t[7]
[$\Phi_3\text{P-OH-NHEt}_2$]ClO ₄	7.31	6.53	3.49	2.91q[7], 1.19t[7]
[$\Phi_3\text{As-OH-NHEt}_2$]ClO ₄	7.43	6.62	3.60	2.56q[7], 1.07t[7]
[$\Phi_3\text{Sb-OH-NHEt}_2$]ClO ₄	(7.45)	6.69	3.71	2.70q[7], 1.03t[7] ^e
[$\Phi_3\text{P-SH-NHEt}_2$]ClO ₄	7.27	6.52	3.53	2.97q[7], 1.23t[7]
[$\Phi_3\text{P-OH-NH}_2^i\text{Bu}$]ClO ₄	7.33	6.54	3.51	2.34d[8], 1.80m, 0.72d[7]
[$\Phi_3\text{As-OH-NH}_2^i\text{Bu}$]ClO ₄	7.42	6.62	3.56	2.21d[7], 1.56m, 0.67d[7]
[$\Phi_3\text{P-OH-piperidine}$]ClO ₄	7.31	6.51	3.51	2.98br, 1.74br, 1.51br
[$\Phi_3\text{As-OH-piperidine}$]ClO ₄	7.42	6.62	3.57	2.75br, 1.59br, 1.45br
[$\Phi_3\text{As-Me}$]I	7.52	6.67	3.62	2.58s
[$\Phi_3\text{Sb-Me}$]I	7.53	6.68	3.66	2.15s
[$\Phi_3\text{As-Et}$]X (X = Br or I)	7.51	6.66	3.63	3.19q[7], 1.22t[8]
[$\Phi_3\text{Sb-Et}$]X (X = Br or I)	7.53	6.68	3.65	2.82q[8], 1.40t[8]
[$\Phi_3\text{As-Bu}$]X (X = Cl, Br or I)	7.51	6.65	3.63	3.14t[7], 1.42m(4H), 0.88t[7]
[$\Phi_3\text{Sb-Bu}$]X (X = Cl, Br or I)	7.53	6.68	3.66	2.78t[8], 1.61m, 1.43m, 0.89t[7]
[$\Phi_3\text{P-CH}_2\text{CH=CH}_2$]ClO ₄	7.52	6.62	3.61	5.63m(1H), 5.0m(2H), 3.95dd[18][7](2H)
[$\Phi_3\text{As-CH}_2\text{CH=CH}_2$]ClO ₄	7.50	6.64	3.63	5.71m(1H), 5.1m(2H), 3.93d[8](2H)
[$\Phi_3\text{Sb-CH}_2\text{CH=CH}_2$]ClO ₄	7.51	6.67	3.66	5.80m(1H), 5.1m(2H), 3.60d[8](2H)
[$\Phi_3\text{P-OMe}$]ClO ₄	7.56	6.63	3.62	3.77d[14]
[$\Phi_3\text{As-OMe}$]I	7.60	6.72	3.67	3.70s
[$\Phi_3\text{P-OEt}$]X (X = Br, I or ClO ₄)	7.57	6.65	3.63	4.07qn[7][7], 1.35dt[1][7]
[$\Phi_3\text{As-OEt}$]X (X = Br or I)	7.58	6.71	3.67	3.88q[7], 1.28t[7]
[$\Phi_3\text{P-OBu}$]I	7.58	6.65	3.63	3.99dt[7][7], 1.67m[7], 1.39m[7], 0.92t[7]
[$\Phi_3\text{As-OBu}$]X (X = Br or I)	7.58	6.71	3.67	3.80t[6], 1.61m[7], 1.37m[7], 0.89t[7]
[$\Phi_3\text{P-OC}_8\text{H}_{17}$]I	7.58	6.65	3.63	3.97dt[7][7], 1.67m[7], 1.25br, 0.86t[7]

^a In CDCl₃ or CD₂Cl₂ at 270 MHz; $\Phi = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$, $\Phi' = 3\text{-Br-}2,6\text{-(MeO)}_2\text{C}_6\text{H}_2$; s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; dd, double doublet; dt, double triplet; m, multiplet; br, broad. The spectral data for $\Phi_3\text{P}$ [1], $\Phi_3\text{PO}$ [2], $\Phi_3\text{PS}$ [7], [$\Phi_3\text{P-SH}$]ClO₄ [7] and [$\Phi_3\text{P-Me}$]I [1] have been reported.

^b Triplet with $J_H = 8\text{--}9$ Hz.

^c Doublet or double doublets with $J_H = 8\text{--}9$ Hz and $J_p = 5\text{--}6$ Hz.

^d Singlet.

^e Suspension in CD₂Cl₂.

and IR spectra in comparison with those of the corresponding iodides.

2.3.3. Reactions with alkyl chlorides

A mixture of $\Phi_3\text{Sb}$ (1 mmol) and butyl chloride (0.5 ml) in methanol (10 ml) was heated at 80°C in a sealed glass tube for 24 h. Volatile materials were removed under reduced pressure, and the residue was extracted with chloroform. Chloroform was removed under reduced pressure, and the residue was washed with benzene to give $[\Phi_3\text{Sb-Bu}]\text{Cl}\cdot x\text{H}_2\text{O}$ with a 24% yield (calculate for $x = 0$) (m.p., 101°C (decomposed)). IR: $\nu(\text{OH})$ 3300 cm^{-1} .

In an analogous manner to the above, $[\Phi_3\text{As-}$

$\text{Bu}]\text{Cl}\cdot x\text{H}_2\text{O}$ was obtained with a 95% yield (calculate for $x = 0$) (m.p., 199–201°C) IR $\nu(\text{OH})$ 3200 and 3290 cm^{-1} .

These compounds were characterized by ^1H NMR and IR spectra in comparison with those of the corresponding iodides.

A mixture of $\Phi_3\text{Sb}$ (1 mmol) and allyl chloride (0.12 ml) in ethanol (10 ml) was heated at 60°C for 9 h. It was diluted with water (15 ml), and 1 M aqueous solution of sodium perchlorate (1.5 ml) was added to give precipitates of $[\Phi_3\text{Sb-CH}_2\text{CH=CH}_2]\text{ClO}_4$ with a 79% yield (m.p., 191°C (decomposed (after recrystallization from ethanol))). IR: $\nu(\text{ClO}_4)$ 1100 cm^{-1} . Anal. Found: C, 47.80; H, 4.81. $\text{C}_{27}\text{H}_{32}\text{ClO}_{10}\text{Sb}$ calc.: C, 48.13; H, 4.79%.

Table 2
 ^{13}C NMR spectral data for some 2,6-dimethoxyphenyl derivatives ^a

Compounds	δ^b (ppm) [J_p (Hz)]
$\Phi_3\text{P}$	116.5 [20], 162.4, 104.3 ^c , 128.3, 55.9
$\Phi_3\text{As}$	– ^d , 162.7, 104.3, 128.3, 55.8
$\Phi_3\text{Sb}$	– ^d , 162.6, 104.2, 128.3, 55.8
$\Phi_3\text{Bi}$	– ^d , 164.4, 104.0, 128.9, 55.5
$\Phi_3\text{AsO}\cdot\text{H}_2\text{O}$	116.9? ^d , 161.7, 104.5, 132.1, 55.9
$\Phi_3\text{SbO}\cdot 3\text{H}_2\text{O}$	119.6? ^d , 161.5, 104.3, 131.4, 55.8
$[\Phi_3\text{P-OH}]\text{X}^e$	– ^d , 162.6, 104.7 ^c , 136.3, 56.4
$[\Phi_3\text{As-OH}]\text{X}^e$	– ^d , 161.2, 105.1, 136.3, 56.6
$[\Phi_3\text{Sb-OH}]\text{X}^e$	108.3? ^d , 162.2, 105.2, 136.7, 56.7
$\Phi_3'\text{PO}\cdot\text{H}_2\text{O}$	122.7 [113], 160.8 and 160.2, 108.7 [10] and 108.3 [8], 135.9, 62.3 and 55.7
$[\Phi_3\text{P-OH-NEt}_3]\text{ClO}_4$	114.6 [117], 162.3, 104.6 ^c , 132.6, 55.8, 46.4, 8.4
$[\Phi_3\text{As-OH-NEt}_3]\text{ClO}_4$	114.8, 161.8, 105.0, 134.0, 56.2, 46.0, 9.3
$[\Phi_3\text{P-SH-NEt}_3]\text{ClO}_4$	116.1 [96], 161.6, 105.1 ^c , 131.3, 55.8, 47.2, 8.8
$[\Phi_3\text{P-OH-NHEt}_2]\text{ClO}_4$	114.6 [119], 162.3, 104.9 ^c , 132.6, 55.9, 43.1, 10.7
$[\Phi_3\text{As-OH-NHEt}_2]\text{ClO}_4$	115.6, 161.5, 105.0, 133.1, 56.0, 42.9, 11.6
$[\Phi_3\text{Sb-OH-NHEt}_2]\text{ClO}_4$	(116.7, 161.7, 104.6, 133.5, 56.0, 43.7, 14.5) ^f
$[\Phi_3\text{P-SH-NHEt}_2]\text{ClO}_4$	115.9 [94], 161.6, 105.3 ^c , 131.6, 55.9, 43.6, 11.0
$[\Phi_3\text{P-OH-piperidine}]\text{ClO}_4$	– ^d , 162.4, 104.8 ^c , 132.6, 55.9, 45.0, 22.5, 21.9
$[\Phi_3\text{As-OH-piperidine}]\text{ClO}_4$	115.1, 161.5, 105.0, 133.4, 56.1, 45.1, 22.7 (overlapped?)
$[\Phi_3\text{As-OH-NH}_2^i\text{Bu}]\text{ClO}_4$	114.1, 161.8, 105.5, 134.3, 56.5, 48.5, 28.6, 20.1
$[\Phi_3\text{As-Me}]\text{I}$	105.6, 161.2, 104.9, 134.9, 56.4, 19.0
$[\Phi_3\text{Sb-Me}]\text{I}$	105.2, 162.4, 104.7, 135.4, 56.4, 7.5
$[\Phi_3\text{As-Et}]\text{I}$	104.6, 161.4, 104.7, 134.8, 56.3, 28.3, 8.7
$[\Phi_3\text{Sb-Et}]\text{I}$	104.3, 162.5, 104.6, 135.3, 56.4, 21.0, 9.4
$[\Phi_3\text{As-Bu}]\text{I}$	– ^d , 161.4, 104.7, 134.8, 56.3, 33.4, 26.1, 24.0, 13.7
$[\Phi_3\text{Sb-Bu}]\text{I}$	104.4, 162.4, 104.7, 135.3, 56.4, 26.8, 25.1 (overlapped?), 13.6
$[\Phi_3\text{P-CH}_2\text{CH=CH}_2]\text{ClO}_4$	100.0 [98], 162.5, 104.6 ^c , 135.7, 56.0, 128.6 [8], 120.7 [16], 33.9 [59]
$[\Phi_3\text{As-CH}_2\text{CH=CH}_2]\text{ClO}_4$	104.9, 161.4, 104.7, 134.9, 56.1, 128.4, 121.8, 38.4
$[\Phi_3\text{Sb-CH}_2\text{CH=CH}_2]\text{ClO}_4$	– ^d , 162.4, 104.7, 135.4, 56.2, 129.1, 120.5, 31.5
$[\Phi_3\text{P-OMe}]\text{ClO}_4$	102.5 [122], 163.0, 104.7 ^c , 136.7, 56.3, 56.9 [9]
$[\Phi_3\text{As-OMe}]\text{I}$	107.0, 161.6, 105.2, 136.4, 56.7, 56.1
$[\Phi_3\text{P-OEt}]\text{ClO}_4$	103.1 [123], 162.9, 104.6 ^c , 136.5, 56.2, 67.3 [9], 16.1 [10]
$[\Phi_3\text{As-OEt}]\text{I}$	107.5, 161.5, 105.2, 136.2, 56.6, 65.0, 17.0
$[\Phi_3\text{As-OBu}]\text{I}$	107.4, 161.5, 105.1, 136.2, 56.5, 68.7, 33.4, 18.9, 13.8

^a In CDCl_3 or CD_2Cl_2 at 68 MHz; $\Phi = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$, $\Phi' = 3\text{-Br-}2,6\text{-(MeO)}_2\text{C}_6\text{H}_2$; in the order of C-1, C-2, C-3,5, C-4, 2,6-MeO and others.

^b Data for $\Phi_3\text{PO}$ [2], $\Phi_3\text{PS}$ [7], $[\Phi_3\text{P-SH}]\text{ClO}_4$ [7] and $[\Phi_3\text{P-Me}]\text{ClO}_4$ [8] have been reported.

^c Doublet with $J_p = 6\text{--}10$ Hz.

^d Very weak or not detected.

^e X = Br, ClO_4 or BF_4 .

^f Suspension in CD_2Cl_2 .

In analogous manners to the above, the following compounds were obtained.

$[\Phi_3P-CH_2CH=CH_2]ClO_4$: 97% yield; m.p., not observed below 240°C (after recrystallization from ethanol). IR: $\nu(ClO_4)$ 1100 cm^{-1} . Anal. Found: C, 55.39; H, 5.61; Cl 6.25. $C_{27}H_{32}ClO_{10}P$ calc.: C, 55.63; H, 5.53; Cl, 6.08%.

$[\Phi_3As-CH_2CH=CH_2]ClO_4$: 98% yield; m.p., not observed below 240°C (after recrystallization from ethanol). IR; $\nu(ClO_4)$ 1100 cm^{-1} . Anal. Found: C, 51.47; H, 5.16. $C_{27}H_{32}AsClO_{10}$ calc.: C, 51.73; H, 5.15%.

2.3.4. Rate measurement

Reaction rates were determined by conductimetry for solutions containing Ar_3M (0.01 M) and alkyl halide (0.20 M) kept in boiling chloroform bath at 61.2°C or boiling benzene bath at 83.5°C. Correlation coefficients were greater than 0.999, except for some very fast reactions with the half-lifetime less than 15 min. Pseudo-first-order rate constants obtained are given in Table 3.

2.4. Reactions of Φ_3M with *N*-bromosuccinimide

2.4.1. Formation of $[\Phi_3M-OH]X$ ($M = P, As$ or Sb ; $X = Br, ClO$ or BF_4)

To a solution of Φ_3As (0.486 g, 1 mmol) in acetone (10 ml, used as purchased) was added dropwise a solution of *N*-bromosuccinimide (NBS) (0.178 g, 1 mmol) in acetone (5 ml), and the mixture was stirred at room temperature for 1 h, resulting in white precipitates of $[\Phi_3As-OH]Br$ (yield 91%; m.p., 199°C (decomposed)). Anal. Found: Br, 13.4. $C_{24}H_{28}O_7AsBr$ calc.: Br, 13.7%. These precipitates were dissolved in water. An addition of 1 M aqueous sodium perchlorate (2 ml) resulted in the precipitation of $[\Phi_3As-OH]ClO_4$ with an 80% yield after recrystallization from ethanol (m.p., not observed below 235°C). Anal. Found: C, 48.08; H, 4.90. $C_{24}H_{28}O_{11}AsCl$ calc: C, 47.82; H, 4.68%. IR; $\nu(OH)$ 3350; $\nu(ClO_4)$ 1100 cm^{-1} .

$[\Phi_3As-OH]ClO_4$ also could be obtained with an 80% yield by the reaction of Φ_3As (1 mmol) and 30% aqueous hydrogen peroxide (0.25 ml, excess) in 2-propanol (30 ml), followed by addition of 60% aqueous perchloric acid (0.15 ml).

In analogous manners to the above, the following compounds were obtained.

$[\Phi_3P-OH]Br$: 90% yield; m.p., 164°C (decomposed).

$[\Phi_3P-OH]ClO_4$: 93% yield; m.p., 230°C (decomposed) (after recrystallization from ethanol). Anal. Found: C, 51.37; H, 5.17; Cl, 6.24. $C_{24}H_{28}O_{11}ClP$ calc.: C, 51.58; H, 5.05; Cl, 6.34% IR: $\nu(OH)$ 3340; $\nu(ClO_4)$ 1100 cm^{-1} .

$[\Phi_3P-OH]BF_4$: 92% yield; m.p., 227°C (decomposed) (after recrystallization from ethanol, followed by drying at 110°C). Anal. Found: C, 52.80; H, 5.13. $C_{24}H_{28}O_7BF_4P$ calc.: C, 52.77; H, 5.17% IR $\nu(OH)$ 3350; $\nu(BF_4)$ 1070 cm^{-1} .

$[\Phi_3Sb-OH]Br$: 85% yield; m.p., 200°C (decomposed).

$[\Phi_3Sb-OH]ClO_4$: 61% yield; m.p., 214°C (decomposed) (after recrystallization from ethanol). Anal. Found: C, 44.30; H, 4.54; Cl, 5.30. $C_{24}H_{28}O_{11}ClSb$ calc.: C, 44.37; H, 4.34; Cl, 5.46% IR; $\nu(OH)$ 3350; $\nu(ClO_4)$ 1100 cm^{-1} .

2.4.2. A reaction of Φ_3Bi

When Φ_3Bi was treated with NBS in an analogous manner to the above, white crystals of 1-bromo-2,6-dimethoxybenzene, (ΦBr) precipitated. When an excess of NBS (3.1 mmol) was used, ΦBr was obtained with a 2.1 mmol yield (m.p., 90–92°C (90–92°C) [9]).

2.4.3. Properties of $[\Phi_3M-OH]X$

$[\Phi_3M-OH]ClO_4$ ($M = P, As$ or Sb) are poorly soluble in water, partially soluble in chloroform but soluble in dichloromethane, and they can be recrystallized from alcohols, acetone or chloroform. $[\Phi_3M-OH]Br$ ($M = P, As$ or Sb) are very soluble in water (1 g in 4–10 ml) and alcohols, and insoluble in non-polar solvents. The

Table 3. Rate constants for the reaction $Ar_3M + RX(excess) \rightarrow [Ar_3M-R]X$

Solvent	RX	Ar_3M	Temperature (°C)	k_1 (s^{-1})	$t_{1/2}$ (min)
MeCN	BuBr	Φ_3P	61.2	Very fast	< 3
		Φ_3As	61.2	1.20×10^{-4}	96
		Φ_3Sb	61.2	3.77×10^{-5}	307
		Φ_3Bi	61.2	No reaction	
		Ph_3P	61.2	$\approx 6.9 \times 10^{-6}$	≈ 1700
EtOH	BuBr	Φ_3As	61.2	6.24×10^{-4}	18.5
		Φ_3Sb	61.2	2.16×10^{-4}	53
	BuI	Φ_3As	61.2	Very fast	< 5
		Ph_3As	61.2	$< 1.72 \times 10^{-5}$	> 670
$ClCH_2CH_2Cl (= RX)$		Φ_3As	83.5	1.23×10^{-4}	94
		Φ_3Sb	83.5	Very slow	–
		Ph_3P	83.5	$\approx 6.8 \times 10^{-6}$	≈ 1700

^a By conductimetry for solutions containing Ar_3M (0.01 M) and RX (0.20 M); $k_{obs} = k_1[RX]$.

aqueous solutions of $[\Phi_3M-OH]Br$ (1×10^{-2} M) showed pH values of 2.09 ($M = P$), 3.79 ($M = As$) and 4.75 ($M = Sb$).

2.5. Isolations of $\Phi_3MO \cdot xH_2O$ ($M = As$ or Sb)

2.5.1. By deprotonation of $[\Phi_3M-OH]ClO_4$

To a suspension of $[\Phi_3As-OH]ClO_4$ (0.602 g, 1 mmol) in water (20 ml) was added 1 M aqueous sodium hydroxide (1.4 ml). The mixture was stirred at room temperature for 0.5 h to give a clear solution. It was extracted with chloroform (40 ml), from which on evaporation was obtained $\Phi_3AsO \cdot H_2O$ with a 94% yield (m.p., 215–219°C). Anal. Found: C, 55.79; H, 5.77. $C_{24}H_{29}O_8As$ calc.: C, 55.39; H, 5.62%; IR: $\nu(OH)$ 3350 broad cm^{-1} .

An analogous treatment of $[\Phi_3Sb-OH]ClO_4$ (0.650 g, 1 mmol) gave crystals of $\Phi_3SbO \cdot 3H_2O$ with a 95% yield (m.p., 195°C (decomposed) (after recrystallization from toluene)). Anal. Found: C, 47.48; H, 5.17. $C_{24}H_{33}O_{10}Sb$ calc.: C, 47.78; H, 5.51% IR: $\nu(OH)$ 3600 very sharp cm^{-1} .

2.5.2. By reaction of Φ_3M with hydrogen peroxide

To a suspension of Φ_3As (0.486 g, 1 mmol) in acetone (5 ml) was added 30% aqueous hydrogen peroxide (0.15 ml, 1.5 mmol). The mixture was stirred at room temperature for 1 h to give a clear solution. Volatile materials were removed under reduced pressure, and the residual solid was crystallized from chloroform as above to give $\Phi_3AsO \cdot H_2O$ with a 74% yield.

An analogous treatment of Φ_3Sb (0.800 g, 1.5 mmol) gave crystals of $\Phi_3SbO \cdot 3H_2O$ with a 96% yield.

When Φ_3Bi was treated in an analogous manner, it was recovered with a 76% yield.

2.6. A reaction of Φ_3PO with *N*-bromosuccinimide

To a solution of Φ_3PO (0.916 g, 2 mmol) in acetone (20 ml) was added dropwise a solution of NBS (8 mmol) in acetone (15 ml). The mixture was stirred at room temperature for 1 h, and it was cooled to $-30^\circ C$ to give white precipitates of $\Phi'_3PO \cdot H_2O$ ($\Phi' = 3-Br-2,6-(MeO)_2C_6H_2$) with a 97% yield (m.p., 186–188°C). Anal. Found: C, 40.11; H, 3.55. $C_{24}H_{26}O_8Br_3P$ calc.: C, 40.42; H, 3.68%. $\Phi'_3PO \cdot H_2O$ is insoluble in water, and the water molecule in the crystals could not be removed on heating at 120°C for 48 h.

2.7. Reactions of $[\Phi_3M-OH]ClO_4$ ($M = P, As$ or Sb) with amines

A mixture of $[\Phi_3P-OH]ClO_4$ (0.559 g, 1 mmol) and triethylamine (0.4–0.8 ml, an excess) in 2-propanol (15 ml) was heated to dissolve. On cooling to $-30^\circ C$, it afforded white crystals of 1:1 adduct $[\Phi_3P-OH-$

$NEt_3]ClO_4$ with an 88% yield. The analytical sample was obtained by recrystallization from 2-propanol (m.p., 202°C (decomposed)). Anal. Found: C, 54.60; H, 6.74; N, 2.08; Cl, 5.46. $C_{30}H_{43}O_{11}ClNP$ calc.: C, 54.59; H, 6.57; N, 2.12; Cl, 5.37% IR: $\nu(ClO_4)$ 1100 cm^{-1} .

In analogous manners to the above, the following adducts were obtained.

$[\Phi_3P-OH-NHEt_2]ClO_4$: 89% yield; m.p., 188°C (decomposed). Anal. Found: C, 53.04; H, 6.33; N, 2.22; Cl, 5.62. $C_{28}H_{39}O_{11}ClNP$ calc.: C, 53.21; H, 6.22; N, 2.22; Cl, 5.61%.

$[\Phi_3P-OH-NBu_3]ClO_4$: 75% yield; m.p., 180–182°C. Anal. Found: C, 57.79; H, 7.60; N, 1.83; Cl, 4.48. $C_{36}H_{55}O_{11}ClNP$ calc.: C, 58.10; H, 7.45; N, 1.88; Cl, 4.76%.

$[\Phi_3P-OH-NH_2^tBu]ClO_4$: 74% yield; m.p., 216°C (decomposed).

$[\Phi_3P-OH-NH_2^iBu]ClO_4$: 78% yield; m.p., 236°C (decomposed). Anal. Found: C, 53.10; H, 6.47; N, 2.22; Cl, 5.64. $C_{28}H_{39}O_{11}ClNP$ calc.: C, 53.21; H, 6.22; N, 2.22; Cl, 5.61%.

$[\Phi_3P-OH-piperidine]ClO_4$: 81% yield; m.p., 182°C (decomposed).

$[\Phi_3P-OH-2,4,6-collidine]ClO_4$: 90% yield; m.p., 183–191°C. Anal. Found: C, 56.21; H, 5.97; N, 1.81; Cl, 5.16. $C_{32}H_{39}O_{11}ClNP$ calc.: C, 56.51; H, 5.78; N, 2.06; Cl, 5.21%.

$[\Phi_3P-OH-4-picoline]ClO_4$: 91% yield; m.p., 156°C (decomposed). Anal. Found: C, 55.22; H, 5.55; N, 1.98; Cl, 5.23. $C_{30}H_{35}O_{11}ClNP$ calc.: C, 55.26; H, 5.41; N, 2.15; Cl, 5.44%.

$[\Phi_3P-OH-3-picoline]ClO_4$: 87% yield; m.p., 159°C (decomposed).

$[\Phi_3P-OH-N-methylimidazole]ClO_4$: 98% yield; m.p., 161°C (decomposed). Anal. Found: C, 52.29; H, 5.53; N, 4.17; Cl, 5.63. $C_{28}H_{34}O_{11}ClNP$ calc.: C, 52.46; H, 5.35; N, 4.37; Cl, 5.53%.

$[(\Phi_3P-OH)_2-NMe_2CH_2CH_2NMe_2](ClO_4)_2$: 54% yield; m.p., 231°C (decomposed). Anal. Found: C, 52.22; H, 6.06; N, 2.28; Cl, 5.55. $C_{54}H_{72}O_{22}Cl_2N_2P_2$ calc.: C, 52.56; H, 5.88; N, 2.27; Cl, 5.75%.

$[\Phi_3As-OH-NEt_3]ClO_4$: 76% yield; m.p., 257°C (decomposed). Anal. Found: C, 50.73; H, 6.13; N, 1.84. $C_{30}H_{43}O_{11}AsClN$ calc.: C, 51.18; H, 6.16; N, 1.19%.

$[\Phi_3As-OH-NHEt_2]ClO_4$: 82% yield; m.p., 260°C (decomposed). Anal. Found: C, 49.24; H, 5.83; N, 2.08. $C_{28}H_{39}O_{11}AsClN$ calc.: C, 49.75; H, 5.82; N, 2.07%.

$[\Phi_3As-OH-NH_2^tBu]ClO_4$: 81% yield; m.p., 257°C (decomposed). Anal. Found: C, 49.67; H, 5.80; N, 2.09. $C_{28}H_{39}O_{11}AsClN$ calc.: C, 49.75; H, 5.82; N, 2.07%.

$[\Phi_3As-OH-piperidine]ClO_4$: 83% yield; m.p., 220°C (decomposed).

$[\Phi_3Sb-OH-NHEt_2]ClO_4$: 70% yield; m.p., 195°C (decomposed).

When $[\Phi_3As-OH]ClO_4$ was treated with tert-butylamine, the crystals contained a small amount of the

amine. When the salt was treated with 3-picoline, 4-picoline, 2,4,6-collidine, *N,N,N',N'*-tetramethylethylenediamine or *N*-methylimidazole, crystals of $[\Phi_3\text{As-OH}]\text{ClO}_4$ were recovered with 50–80% yields.

When $[\Phi_3\text{Sb-OH}]\text{ClO}_4$ was treated with triethylamine, isobutylamine or *N*-methylimidazole, the crystals contained small amounts of the amines. When the salt was treated with 3-picoline, 4-picoline, 2,4,6-collidine, *N,N,N',N'*-tetramethylethylenediamine or piperidine, crystals of $[\Phi_3\text{Sb-OH}]\text{ClO}_4$ were recovered with 50–80% yields.

2.8. Reactions of $[\Phi_3\text{P-SH}]\text{ClO}_4$ with amines

Since $[\Phi_3\text{P-SH}]\text{ClO}_4$ desulfurizes in hot solutions [2], it was treated with amines in analogous manners to the above but by minimum heating; the following 1:1 adducts were obtained as crystals.

$[\Phi_3\text{P-SH-NEt}_3]\text{ClO}_4$: 91% yield; m.p., 129°C (decomposed). Anal. Found: C, 53.06; H, 6.43; N, 2.07. $\text{C}_{30}\text{H}_{43}\text{O}_{10}\text{ClNPS}$ calc.: C, 53.29; H, 6.41; N, 2.07%.

$[\Phi_3\text{P-SH-NHET}_2]\text{ClO}_4$: 87% yield; m.p., 157°C (decomposed). Anal. Found: C, 51.52; H, 6.08; N, 2.16. $\text{C}_{28}\text{H}_{39}\text{O}_{10}\text{ClNPS}$ calc.: C, 51.89; H, 6.06; N, 2.16%.

$[\Phi_3\text{P-SH-4-picoline}]\text{ClO}_4$: 88% yield; m.p., 153°C (decomposed). Anal. Found: C, 53.80; H, 5.33; N, 1.99. $\text{C}_{30}\text{H}_{35}\text{O}_{10}\text{ClNPS}$ calc.: C, 53.93; H, 5.28; N, 2.10%.

$[\Phi_3\text{P-SH-3-picoline}]\text{ClO}_4$: 91% yield; m.p., 125°C (decomposed). Anal. Found: C, 53.79; H, 5.38; N, 1.99. $\text{C}_{30}\text{H}_{35}\text{O}_{10}\text{ClNPS}$ calc.: C, 53.93; H, 5.28; N, 2.10%.

$[\Phi_3\text{P-SH-2,4,6-collidine}]\text{ClO}_4$: 93% yield; m.p., 157°C (decomposed). Anal. Found: C, 55.15; H, 5.65; N, 2.04. $\text{C}_{32}\text{H}_{39}\text{O}_{10}\text{ClNPS}$ calc.: C, 55.21; H, 5.65; N, 2.01%.

When $[\Phi_3\text{P-SH}]\text{ClO}_4$ was treated with $^i\text{BuNH}_2$, $^i\text{BuNH}_2$, *N,N,N',N'*-tetramethylethylenediamine, piperidine and *N*-methylimidazole, crystals of $\Phi_3\text{PS}$ were obtained with 90–95% yields.

2.9. Reactions of $\Phi_3\text{MO}$ to give $[\Phi_3\text{M-OR}]\text{X}$

2.9.1. Reactions of $\Phi_3\text{PO}$ with dialkyl sulfates

A mixture of $\Phi_3\text{PO}$ (0.458 g, 1 mmol) and dimethyl sulfate (0.4 ml) was heated at 55°C for 1 h. It was dissolved in 2-propanol (3 ml), and 1 M aqueous sodium perchlorate (2 ml) was added to give white precipitates. The suspension was warmed to give an almost clear solution, a small amount of insoluble material was removed by filtration, and the filtrate was cooled to –30°C to give white crystals of $[\Phi_3\text{P-OMe}]\text{ClO}_4$ with an 89% yield (m.p., not observed below 240°C after recrystallization from ethanol). Anal. Found: C, 52.19; H, 5.27. $\text{C}_{25}\text{H}_{30}\text{O}_{11}\text{ClP}$ calc.: C, 52.41; H, 5.28%.

In an analogous manner to the above, $[\Phi_3\text{P-OEt}]\text{ClO}_4$ was obtained with an 89% yield (m.p., not observed below 240°C after recrystallization from

ethanol). Anal. Found: C, 52.90; H, 5.54. $\text{C}_{26}\text{H}_{32}\text{O}_{11}\text{ClP}$ calc.: C, 53.20; H, 5.50%.

2.9.2. Reactions of $\Phi_3\text{MO}\cdot x\text{H}_2\text{O}$ with alkyl iodides

The crystals of $\Phi_3\text{PO}$ (0.458 g, 1 mmol) was heated in neat butyl iodide (5 ml) at 80°C for 1 h to give the crystals of $[\Phi_3\text{P-OBu}]\text{I}$ with an 85% yield (m.p., 130°C (decomposed)).

To a solution of $\Phi_3\text{AsO}\cdot x\text{H}_2\text{O}$, prepared in situ from $\Phi_3\text{As}$ (1 mmol) and 30% aqueous hydrogen peroxide in 2-propanol (15 ml) as above, was added ethyl iodide (0.5 ml). The mixture was stirred for 2 h at room temperature and for 10 min at 60°C to dissolve the fine precipitates, and it was cooled to –30°C to give brown crystals of $[\Phi_3\text{As-OEt}]\text{I}$ with an 80% yield (m.p., 210°C (decomposed)).

The crystals of $[\Phi_3\text{As-OEt}]\text{I}$ (0.658 g, 1 mmol) were dissolved in 2-propanol (50 ml) at 80°C, and aqueous 1 M sodium perchlorate (2 ml) was added. The mixture was filtered while hot, and the filtrate was cooled to –30°C to give white crystals of $[\Phi_3\text{As-OEt}]\text{ClO}_4$ with a 96% yield (m.p., 246°C (decomposed)). Anal. Found: C, 49.21; H, 5.11. $\text{C}_{26}\text{H}_{32}\text{O}_{11}\text{AsCl}$ calc.: C, 49.50; H, 5.11%.

In analogous manners to the above, the following compounds were obtained.

$[\Phi_3\text{As-OMe}]\text{I}$: 93% yield; m.p., 203°C (decomposed).

$[\Phi_3\text{As-OMe}]\text{ClO}_4$: 93% yield; m.p., 240°C (decomposed). Anal. Found: C, 48.45; H, 4.91. $\text{C}_{25}\text{H}_{30}\text{O}_{11}\text{AsCl}$ calc.: C, 48.68; H, 4.90%.

$[\Phi_3\text{P-OEt}]\text{I}$: 86% yield; m.p., 203°C (decomposed).

$[\Phi_3\text{As-OBu}]\text{I}$: 80% yield; m.p., 186°C (decomposed). Anal. Found: C, 48.77; H, 5.34. $\text{C}_{28}\text{H}_{36}\text{O}_7\text{AsI}$ calc.: C, 49.00; H, 5.29%.

$[\Phi_3\text{P-OC}_8\text{H}_{17}]\text{I}$: 78% yield; m.p., 183°C (decomposed).

Attempts of recrystallization of $[\Phi_3\text{P-OR}]\text{I}$ resulted in partial decomposition to give $\Phi_3\text{PO}$.

An analogous treatment of $\Phi_3\text{SbO}\cdot x\text{H}_2\text{O}$ with ethyl iodide resulted in $[\Phi_3\text{Sb-OH}]\text{I}$ with an 82% yield.

2.9.3. Reactions of $\Phi_3\text{MO}\cdot x\text{H}_2\text{O}$ with alkyl bromides

The crystals of $\Phi_3\text{PO}$ (0.458 g, 1 mmol) was heated in neat ethyl bromide (5 ml) at 80°C for 1.5 h to give the crystals of $[\Phi_3\text{P-OEt}]\text{Br}$ with a 72% yield (m.p., 149°C (decomposed)). Attempts at recrystallization of $[\Phi_3\text{P-OEt}]\text{Br}$ resulted in partial decomposition to give $\Phi_3\text{PO}$.

To a solution of $\Phi_3\text{AsO}\cdot x\text{H}_2\text{O}$, prepared in situ from $\Phi_3\text{As}$ (1 mmol) and 30% aqueous hydrogen peroxide in 2-propanol (30 ml) as above, was added ethyl bromide (0.3 ml) at 60°C. The mixture was stirred for 5 h at room temperature, the volatile materials were removed under reduced pressure, and the residue was washed with benzene to give light-yellow crystals of

$[\Phi_3\text{As}-\text{OEt}]\text{Br}$ with a 90% yield (m.p., 209°C (decomposed)).

In an analogous manner to the above, $[\Phi_3\text{As}-\text{OBu}]\text{Br}$ was obtained with a 78% yield (m.p., 170°C (decomposed)).

These compounds were characterized by ^1H NMR and IR spectra in comparison with those of the corresponding iodides.

2.10. Reactions of Φ_3M with $[\Phi_3M'-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ ($M, M' = \text{P, As or Sb}$)

Solutions containing Φ_3M and $[\Phi_3M'-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ (1:1 mole ratio) in acetone- d_6 were heated at 80°C in a sealed NMR glass tube, and the ^1H NMR spectra were measured to detect the reaction products.

A mixture of $\Phi_3\text{P}$ and $[\Phi_3\text{As}-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ heated for 20 h showed the formation of $[\Phi_3\text{P}-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ and $\Phi_3\text{As}$ with 8–10% yields.

A mixture of $\Phi_3\text{P}$ and $[\Phi_3\text{Sb}-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ heated for 10 h showed the formation of $[\Phi_3\text{P}-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ and $\Phi_3\text{Sb}$ with 85–90% yields.

A mixture of $\Phi_3\text{As}$ and $[\Phi_3\text{Sb}-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ heated for 40 h showed the formation of $[\Phi_3\text{As}-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ and $\Phi_3\text{Sb}$ with 35–40% yields.

Mixtures of $\Phi_3\text{Sb}$ and $[\Phi_3M-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ ($M = \text{P or As}$) heated for 40 h showed no new product.

3. Results and discussion

3.1. Some basic properties of tris(2,6-dimethoxyphenyl)arsine, tris(2,6-dimethoxyphenyl)stibine and tris(2,6-dimethoxyphenyl)bismuthine (Φ_3M ($M = \text{As, Sb and Bi}$) respectively)

While $\Phi_3\text{As}$ and $\Phi_3\text{Sb}$ prepared in the present work showed similar physical properties to those reported by Horner and Simons [4], the melting point of $\Phi_3\text{Bi}$ was much higher than reported [4]. $\Phi_3\text{Bi}$ is stable in hot benzene- d_6 with little decomposition during 2 days at 80°C, but it decomposes in hot alcohols to give 1,3-dimethoxybenzene. The other Φ_3M ($M = \text{P, As or Sb}$) suffer air oxidation in hot alcohols.

Both $\Phi_3\text{As}$ and $\Phi_3\text{Sb}$ reacted very easily with common alkyl iodides ($\text{RI} = \text{MeI, EtI or BuI}$) in benzene at room temperature to give $[\Phi_3\text{As}-\text{R}]\text{I}$ and $[\Phi_3\text{Sb}-\text{R}]\text{I}$ respectively, but $\Phi_3\text{Bi}$ was recovered with an 86% yield from a solution containing ethyl iodide heated at 80°C for 15 h. $\Phi_3\text{As}$ reacted also with alkyl bromides ($\text{RBr} = \text{EtBr or BuBr}$) in hot benzene or methanol. $\Phi_3\text{Sb}$ was poorly reactive with these bromides in benzene, but it reacted in hot methanol to give $[\Phi_3\text{Sb}-\text{R}]\text{Br}$. Both $\Phi_3\text{As}$ and $\Phi_3\text{Sb}$ reacted even with butyl chloride in hot methanol, although the yield of $[\Phi_3\text{Sb}-\text{Bu}]\text{Cl}$ was poor after 24 h at 80°C. Since the IR spectra of

these chlorides $[\Phi_3M-\text{R}]\text{Cl}$ show bands attributable to $\nu(\text{OH})$, they must be hydrated, and they are quite soluble in water. Allyl chloride reacted with Φ_3M ($M = \text{P, As or Sb}$) in hot ethanol, the products were very hygroscopic, and they were derived to isolate in the form of perchlorates $[\Phi_3M-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$. The allyl group exchange was observed between $\Phi_3\text{P}$ and $[\Phi_3M-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ ($M = \text{As or Sb}$) and between $\Phi_3\text{As}$ and $[\Phi_3\text{Sb}-\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ in hot acetone, although the reactions were very slow at 80°C.

Comparison of the reaction rates (Table 3) indicates that, while the reactivity with butyl halides decreases in the order $\Phi_3\text{P} > \Phi_3\text{As} > \Phi_3\text{Sb} > \Phi_3\text{Bi}$, both $\Phi_3\text{As}$ and $\Phi_3\text{Sb}$ are much more reactive than triphenylphosphine or triphenylarsine in spite of the steric bulkiness of the Φ group.

3.2. Oxidation of tris(2,6-dimethoxyphenyl)arsine, tris(2,6-dimethoxyphenyl)stibine and tris(2,6-dimethoxyphenyl)bismuthine

Treatment of Φ_3M ($M = \text{P, As or Sb}$) with a stoichiometric amount of NBS in aqueous acetone resulted in the precipitation of the hydroxyonium bromides $[\Phi_3M-\text{OH}]\text{Br}$. On the contrary, an analogous treatment of $\Phi_3\text{Bi}$ with NBS resulted in decomposition to give 1-bromo-2,6-dimethoxybenzene (ΦBr). An analogous reaction to give ΦBr has been reported for a tin compound $\text{Me}_2\Phi_2\text{Sn}$, which was found to be a selective preparative intermediate for ΦX ($\text{X} = \text{Cl, Br and I}$) [9]. The $[\Phi_3M-\text{OH}]\text{Br}$ compounds are highly soluble in water to afford acidic solutions, and treatment of $[\Phi_3M-\text{OH}]\text{Br}$ with perchloric acid in water gave precipitation of the perchlorates $[\Phi_3M-\text{OH}]\text{ClO}_4$. Hydroxytriphenylphosphonium and arsonium salts $[\text{Ph}_3M-\text{OH}]\text{X}$ have long been known, although the isolation of phosphonium salts is not always easy [10–13]. In contrast, it has been known that attempts to prepare compounds of types $[\text{R}_3\text{Sb}-\text{OH}]\text{X}$ or $\text{R}_3\text{Sb}(\text{OH})\text{X}$ result in an oxygen bridged compound $(\text{R}_3\text{SbX})_2\text{O}$, except for compounds bearing bulky substituent such as $\text{R} = \text{cyclohexyl}$ [14,15]. Although antimony atom can adopt such a five-coordination [15], it must be improbable for $[\Phi_3\text{Sb}-\text{OH}]\text{Br}$ owing to the bulkiness of the Φ group. In fact, identical chemical shifts were observed in the ^1H NMR spectra of $[\Phi_3\text{Sb}-\text{OH}]\text{Br}$ and $[\Phi_3\text{Sb}-\text{OH}]\text{ClO}_4$. The Brønsted acidity of $[\text{Ph}_3\text{P}-\text{OH}]\text{X}$ is known to be stronger than that of $[\text{Ph}_3\text{As}-\text{OH}]\text{X}$ [12]. From the pH measurements of aqueous solutions, the acidities of $[\Phi_3M-\text{OH}]\text{Br}$ were found to decrease in the order $M = \text{P} > \text{As} > \text{Sb}$.

Treatment of $[\Phi_3\text{As}-\text{OH}]\text{ClO}_4$ with aqueous sodium hydroxide gave the oxide as the hydrate $\Phi_3\text{AsO} \cdot x\text{H}_2\text{O}$. The elemental analyses of crystals obtained from chloroform agreed best with the monohydrate $\Phi_3\text{AsO} \cdot \text{H}_2\text{O}$. $\Phi_3\text{PO}$ [2] and Ph_3AsO [11] have been obtained also as

the hydrate, and these compounds dehydrate easily on heating. However, $\Phi_3\text{As}\cdot\text{H}_2\text{O}$ is quite inert to dehydration. In an analogous manner, the stibine oxide $\Phi_3\text{SbO}\cdot x\text{H}_2\text{O}$ could be obtained, and the elemental analyses agreed best with the trihydrate $\Phi_3\text{SbO}\cdot 3\text{H}_2\text{O}$. These oxides also could be obtained by the reaction of $\Phi_3\text{M}$ with hydrogen peroxide; they are soluble in water, and treatment of the aqueous solution with perchloric acid gave $[\Phi_3\text{M}-\text{OH}]\text{ClO}_4$. The precise formulations of these oxides are not known at present. Ferguson and Macaulay [16] have shown that the crystal structure of $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ comprises discrete centrosymmetric dimers with each water molecule hydrogen bonded to two oxygen atoms of triphenylarsine oxide. Since hydroxy group is smaller than bromide, a five-coordinate formulation such as $\Phi_3\text{Sb}(\text{OH})_2\cdot 2\text{H}_2\text{O}$ is possible for $\Phi_3\text{SbO}\cdot 3\text{H}_2\text{O}$. A possibility of a polymeric structure having an $\text{Sb}-\text{O}-\text{Sb}$ bond may be disregarded owing to the bulkiness of the Φ group.

When $\Phi_3\text{Bi}$ was treated with hydrogen peroxide in an analogous manner to above, it was recovered or it decomposed under more forcing conditions. In contrast with $\Phi_3\text{P}$ [7], $\Phi_3\text{M}$ ($\text{M} = \text{As}$ or Sb) did not react with elemental sulfur.

A treatment of $\Phi_3\text{PO}$ with an excess of NBS in acetone resulted in the bromination at the 3-position of Φ groups to give $\Phi'_3\text{PO}\cdot\text{H}_2\text{O}$ ($\Phi' = 3\text{-Br-2,6-(MeO)}_2\text{C}_6\text{H}_2$). In contrast with $\Phi_3\text{PO}$, $\Phi'_3\text{PO}\cdot\text{H}_2\text{O}$ is insoluble in water and does not react with perchloric acid. The weaker basicity of $\Phi'_3\text{PO}\cdot\text{H}_2\text{O}$ than $\Phi_3\text{PO}$ may be explained in terms of the "buttressing effect" [17]; the presence of large bromine atom at 3-position may force the 2-methoxy methyl group to orient closer to the phosphorus atom, where the oxygen lone pairs have less possibility to interact with the phenyl ring or with phosphorus atom, resulting in the lower electron density on the $\text{P}=\text{O}$ group.

3.3. Formation of amine adducts

Triphenylphosphine oxide has long been known to cocrystallize with a wide variety of molecules by hydrogen bonding, such as water, acids, triphenylmethanol, phenols, carboxylic acids and diaryl ureas [12,18–22]. Recently, a closely related adduct has been reported [23], where a mixture of Ph_3PO , tetrafluoroboric acid and *N,N*-dimethyl-*o*-phenylenediamine formed the 1:1:1 adduct. The crystal structure revealed that the amine is protonated on the dimethylamino group, acting as a bidentate chelating agent through two hydrogen bonds with the oxygen of Ph_3PO [23]. Related adducts with primary amines have also been reported for a macrocycle having a triarylphosphine oxide moiety [24]. We have found that $[\Phi_3\text{P}-\text{OH}]\text{ClO}_4$ reacted with triethylamine ($\text{p}K_a = 10.72$) in 2-propanol to give their 1:1 adduct $[\Phi_3\text{P}-\text{OH}-\text{NEt}_3]\text{ClO}_4$ rather than the deprotonated product $\Phi_3\text{PO}$ [5].

The same adduct was obtained also by the reaction of $\Phi_3\text{PO}$ and triethylammonium perchlorate. The $\nu(\text{OH})$ band of $[\Phi_3\text{P}-\text{OH}]\text{ClO}_4$ observed at 3340 cm^{-1} in the IR spectrum was absent in the spectrum of the adduct, and no band attributable to $\nu(\text{O}-\text{H}-\text{N})$ was observed in the region $3000\text{--}1800\text{ cm}^{-1}$. Analogous 1:1 adducts were obtained with a wide variety of amines such as piperidine ($\text{p}K_a = 11.12$), diethylamine ($\text{p}K_a = 10.93$), tributylamine ($\text{p}K_a = 10.89$), tert-butylamine ($\text{p}K_a = 10.45$), iso-butylamine ($\text{p}K_a = 10.41$), 2,4,6-collidine ($\text{p}K_a = 7.43$), *N*-methylimidazole ($\text{p}K_a = 6.95$), 4-picoline ($\text{p}K_a = 6.04$), 3-picoline ($\text{p}K_a = 5.76$) and *N,N,N',N'*-tetramethylethylenediamine (2:1 adduct). These adducts could be recrystallized from 2-propanol. While analogous amine adducts were obtained for $[\Phi_3\text{As}-\text{OH}]\text{ClO}_4$ on treatment with excess of amines such as triethylamine, diethylamine, isobutylamine and piperidine, most of them were unstable, decomposing to $[\Phi_3\text{As}-\text{OH}]\text{ClO}_4$ during recrystallization. $[\Phi_3\text{Sb}-\text{OH}]\text{ClO}_4$ formed much less stable adducts with these amines, or it did not form at all. $[\Phi_3\text{P}-\text{SH}]\text{ClO}_4$ formed stable adducts with triethylamine, diethylamine, 2,4,6-collidine, 4-picoline and 3-picoline, which can be recrystallized from 2-propanol. However, the reactions of $[\Phi_3\text{P}-\text{SH}]\text{ClO}_4$ with piperidine, tert-butylamine, isobutylamine, *N*-methylimidazole and *N,N,N',N'*-tetramethylethylenediamine resulted in an unstable adduct or deprotonated product, $\Phi_3\text{PS}$. Again, the $\nu(\text{S}-\text{H})$ band of $[\Phi_3\text{P}-\text{SH}]\text{ClO}_4$ (2510 cm^{-1}) was absent in the IR spectrum of $[\Phi_3\text{P}-\text{SH}-\text{NEt}_3]\text{ClO}_4$, and no band attributable to $\nu(\text{S}-\text{H}-\text{N})$ was observed.

3.4. Reactions of tris(2,6-dimethoxyphenyl)phosphine oxide, tris(2,6-dimethoxyphenyl)arsine oxide and tris(2,6-dimethoxyphenyl)stibine oxide with alkyl halides

$\Phi_3\text{PO}$ reacted in dialkyl sulfates (Me_2SO_4 and Et_2SO_4) or in neat alkyl halides ($\text{RX} = \text{EtI}$, BuI , $\text{C}_8\text{H}_{17}\text{I}$ or EtBr) to give the alkoxyphosphonium salts $[\Phi_3\text{P}-\text{OR}]\text{X}$. When the reactions with these alkyl halides were performed in 2-propanol, the yields were very poor. It was soon found that the reactions were reversible, and these halide salts partly decomposed in alcohols. However, the perchlorates $[\Phi_3\text{P}-\text{OR}]\text{ClO}_4$ are stable in a variety of solutions, and they could be recrystallized from alcohols without hydrolysis or alcoholysis. $\Phi_3\text{AsO}\cdot\text{H}_2\text{O}$ reacted with alkyl iodides and bromides even in 2-propanol to give $[\Phi_3\text{As}-\text{OR}]\text{X}$ ($\text{RX} = \text{MeI}$, EtI , BuI , EtBr or BuBr) with much better yields, while it was poorly reactive with butyl chloride. The $[\Phi_3\text{As}-\text{OR}]\text{X}$ compounds are more stable than $[\Phi_3\text{P}-\text{OR}]\text{ClO}_4$ in alcohols. Interestingly, preliminary experimentals showed that $[\Phi_3\text{As}-\text{OR}]\text{ClO}_4$ decomposed more easily in acidic solutions to give $[\Phi_3\text{As}-\text{OH}]\text{ClO}_4$ than did $[\Phi_3\text{P}-\text{OR}]\text{ClO}_4$. $\Phi_3\text{SbO}\cdot 3\text{H}_2\text{O}$ reacted with ethyl io-

dide in 2-propanol to give $[\Phi_3\text{Sb-OH}]\text{I}$, a product formed probably by the hydrolysis of $[\Phi_3\text{Sb-OEt}]\text{I}$ or ethyl iodide. Attempts to prepare $[\Phi_3\text{Sb-OR}]\text{X}$ by reaction of $\Phi_3\text{Sb}$ with NBS in alcohols also resulted in $[\Phi_3\text{Sb-OH}]\text{X}$.

3.5. ^1H and ^{13}C NMR spectra

The ^1H NMR spectra of $\Phi_3\text{M}$ derivatives ($\text{M} = \text{As}, \text{Sb}$ or Bi) (Table 1) show a triplet due to 4-protons, a doublet due to 3,5-protons and a very sharp singlet due to 2,6-methoxy protons, indicating the presence of free rotation of Φ group around the C–M bonds. The 3,5-proton resonance of $\Phi_3\text{P}$ derivatives appears as double doublets owing to the presence of magnetic coupling (8–9 Hz) with the phosphorus atom. The 4-proton resonance of the Φ group is the most sensitive to the change in the type of compound. It shifts to lower magnetic field in the order $\Phi_3\text{M}$ (7.11–7.14 ppm) < $\Phi_3\text{MO}\cdot x\text{H}_2\text{O}$ (7.23–7.35 ppm) < $[\Phi_3\text{M-OH-amine}]\text{ClO}_4$ (7.31–7.45 ppm) < $[\Phi_3\text{M-R}]\text{X}$ (7.50–7.53 ppm) < $[\Phi_3\text{M-OH}]\text{X}$ (7.50–7.59 ppm) \approx $[\Phi_3\text{M-OR}]\text{X}$ (7.56–7.58 ppm). A related order has been observed for the derivatives of phosphine sulfide: $\Phi_3\text{P}$ (7.12 ppm [1]) < $\Phi_3\text{PS}$ (7.22 ppm [7]) < $[\Phi_3\text{P-SH-amine}]\text{ClO}_4$ < $[\Phi_3\text{P-SH}]\text{ClO}_4$ (7.56 ppm [7]) \approx $[\Phi_3\text{P-SEt}]\text{ClO}_4$ (7.58 ppm [7]). The analogous orders can be observed also for 3,5-protons and for 2,6-methoxy protons although less sensitive. These chemical shifts seem to reflect the positive character order of $\Phi_3\text{M}$ moieties of these compounds. In most types of compound bearing the M–O bond, these resonances are sensitive to the change in the element M. In general, the resonances are observed at a lower magnetic field in the order $\text{M} = \text{P} < \text{As} < \text{Sb}$, which is the reverse order expected from the electronegativity. The chemical shifts of amine protons of $[\Phi_3\text{M-YH-amine}]\text{ClO}_4$ ($\text{Y} = \text{O}$ or S) are also shown in Table 1 for the representative compounds, the shift order varying considerably depending on the compound. The resonances of alkoxy protons of $[\Phi_3\text{P-OR}]\text{X}$ are observed at lower magnetic fields than those of $[\Phi_3\text{As-OR}]\text{X}$. While it can be explained by the more electronegative property of phosphorus atom, such an explanation cannot be applied to the chemical shifts of alkyl protons of $[\Phi_3\text{M-R}]\text{X}$. The α -protons of $[\Phi_3\text{P-OR}]\text{X}$ are magnetically coupled with the phosphorus atom.

The ^{13}C NMR spectra of $\Phi_3\text{M}$ derivatives (Table 2) show five resonances due to Φ -group carbon atoms. The *ipso*-carbon (C(1)) resonance of the Φ group is often too weak to be observed, and the resonance of $\Phi_3\text{P}$ derivatives is split into a doublet with a varying coupling constant with ^{31}P . The coupling constant is the smallest for $\Phi_3\text{P}$ (20 Hz) and is very large for four-coordinated species: $[\Phi_3\text{P-H}]^+$ (105 Hz [7]), $\Phi_3\text{PO}$ (115 Hz [2]), $[\Phi_3\text{P-OH-NEt}_3]^+$ (117 Hz) and $[\Phi_3\text{P-OEt}]^+$ (122 Hz). The chemical shift varies in a region between

95 ppm (for $[\Phi_3\text{P-H}]^+$ [7]) and 120 ppm, and there seems no clear difference between cationic and neutral compounds. The *ortho*-carbon (C(2,6)) resonance of $\Phi_3\text{M}$ derivatives is observed at a low magnetic field as 161–163 ppm owing to the presence of the methoxy substituent. The order of chemical shifts is not in accord with the order of elements. The *meta*-carbon (C(3,5)) resonance of $\Phi_3\text{P}$ derivatives is also observed as doublet with a small coupling constant ($J_p = 6\text{--}10$ Hz). The chemical shift is observed in very narrow regions depending on the type of compound: $\Phi_3\text{M}$ (128–129 ppm), $\Phi_3\text{MO}\cdot x\text{H}_2\text{O}$ (131–132 ppm), $[\Phi_3\text{M-OH}]^+$ (136–137 ppm), $[\Phi_3\text{M-OH-amine}]^+$ (132–135 ppm), $[\Phi_3\text{M-R}]^+$ (134–136 ppm) and $[\Phi_3\text{M-OR}]^+$ (136–137 ppm). The 2,6-methoxy carbon resonance of $\Phi_3\text{M}$ derivatives ($\text{M} = \text{P}, \text{As}$ or Sb) is observed in the narrow region 56.2 ± 0.5 ppm, and the resonances of alkoxy carbon atoms of $[\Phi_3\text{P-OR}]\text{ClO}_4$ are observed as a doublet owing to the presence of magnetic coupling with the phosphorus atom.

Acknowledgment

This work was supported by the Grant-in-Aid for Scientific Research 04555207 from the Ministry of Education, Science and Culture.

References

- [1] M. Wada, S. Higashizaki and A. Tsuboi, *J. Chem. Res. S.* (1985) 38; *J. Chem. Res. M.*, (1985) 467.
- [2] M. Wada, T. Fujii, S. Iijima, S. Hayase, T. Erabi and G. Matsubayashi, *J. Organomet. Chem.*, 445 (1993) 65.
- [3] M. Wada, M. Kanzaki, H. Ogura, S. Hayase and T. Erabi, *J. Organomet. Chem.*, 485 (1995) 127.
- [4] L. Horner and G. Simons, *Phosphorus Sulfur*, 14 (1983) 253.
- [5] M. Wada, H. Ohta, N. Hashizume, M. Kanzaki, K. Hirata and T. Erabi, *Chem. Express*, 3 (1988) 471.
- [6] M. Wada, S. Hayashi, S. Miyake, S. Hayase and T. Erabi, *Chem. Express*, 7 (1992) 693.
- [7] M. Wada, M. Kanzaki, M. Fujiwara, K. Kajihara and T. Erabi, *Bull. Chem. Soc. Jpn.*, 64 (1991) 1782.
- [8] M. Wada and A. Tsuboi, *J. Chem. Soc., Perkin Trans. I.*, (1987) 151.
- [9] M. Wada, H. Wakamori, A. Hiraiwa and T. Erabi, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1389.
- [10] M.H. O'Brien, G.O. Doak and G.G. Long, *Inorg. Chim. Acta*, 1 (1967) 34.
- [11] G.S. Harris and F. Inglis, *J. Chem. Soc. A.*, (1967) 497.
- [12] D. Hadzi, C. Klofutar and S. Oblak, *J. Chem. Soc. A.*, (1968) 905.
- [13] G. Ferguson and E.W. Macaulay, *J. Chem. Soc. A.*, (1969) 1.
- [14] G.C. Tranter, C.C. Addison and D.B. Sowerby, *J. Organomet. Chem.*, 12 (1968) 369.
- [15] Y. Kawasaki, Y. Yamamoto and M. Wada, *Bull. Chem. Soc. Jpn.*, 56 (1983) 145.
- [16] G. Ferguson and E.W. Macaulay, *J. Chem. Soc., Chem. Commun.*, (1968) 1288.

- [17] H. Tomioka, K. Kimoto, H. Murata and Y. Izawa, *J. Chem. Soc., Perkin Trans. I*, (1991) 471, and references cited therein.
- [18] P.W. Baures, *Acta Crystallogr., Sect. C47* (1991) 2715.
- [19] E.M. Arnett, E.J. Mitchell and T.S.S.R. Murty, *J. Am. Chem. Soc.*, *96* (1974) 3875.
- [20] Von D. Thierbach and F. Huber, *Z. Anorg. Allg. Chem.*, *477* (1981) 101.
- [21] C. Lariucci, R.H.A. Santos and J.R. Lechat, *Acta Crystallogr., Sect. C42* (1986) 1825.
- [22] M.C. Etter and S.M. Reutzel, *J. Am. Chem. Soc.*, *113* (1991) 2586, and references cited therein.
- [23] A.L. Llamas-Saiz, C. Foces-Foces, J. Elguero, P. Molina, M. Alajarin and A. Vidal, *J. Chem. Soc., Chem. Commun.*, (1991) 1694.
- [24] P.B. Savage, S.K. Holmgren and S.H. Gellman, *J. Am. Chem. Soc.*, *115* (1993) 7900; P.B. Savage and S.H. Gellman, *J. Am. Chem. Soc.*, *115* (1993) 10448.