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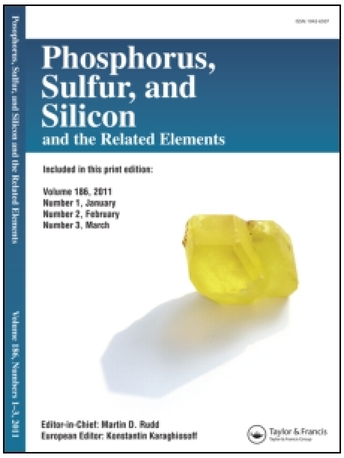

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SYNTHESIS AND CHARACTERIZATION OF PHOSPHINIC AND PHOSPHATE COMPLEXES OF GALLIUM(III) AND INDIUM(III)

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SYNTHESIS AND CHARACTERIZATION OF PHOSPHINIC AND PHOSPHATE COMPLEXES OF GALLIUM(III) AND INDIUM(III)

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Gallium(III)/Indium(III) complexes of the type $[GaCl_N(O_2PPh_2)_{3-N}]$, $[GaCl_N\{O_2P(OBu^{n/t})_2\}_{3-N}]$ and $[In(O_2PR_2)_3]$ (R = Ph or OBu^n) (where N = 0, 1 or 2) were synthesized by the reactions of $GaCl_3/InCl_3$ with Ph_2POONa or $[(Bu^{n/t}O)_2POOK/1/2Pb]$ or $[(Bu^nO)_2POOH]$ and Et_3N in benzene. They were characterized by elemental analysis, IR and NMR(^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) data. *Keywords*: Gallium, Indium, Diphenylphosphinates, Dibutylphosphates, IR spectra, NMR spectra.

INTRODUCTION

There is an increasing interest in metal phosphates due to their relevance in biology and materials science[1,2] as they imitate zeolites. The chemistry of oxy- and thiophosphate ligands has received considerable attention in recent years[3]. The stereochemistry of these molecules shows remarkable variation from discrete monomeric units to associated or supramolecular structures[3b–3f]. The organotin chemistry with these ligands also demonstrated that this class of ligands are excellent candidates to stabilize diverse stereochemistries of organotins[3]. Except a few organogallium/indium complexes with oxyphosphorous acids, much attention was focussed on thiophosphorous ligands[4–10]. Organogallium complexes with phosphinic acids are mostly dimeric molecules, e.g.

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$[\{Bu^t_2Ga(\mu\text{-}O_2PPh_2)\}_2]$[11] and $[\{Me_2Ga(O_2PPh_2)\}_2]$[12]. The organoindium complexes with phosphinic acids are associated molecules which are either dimeric, such as $[\{Me_2In(O_2PPh_2)\}_2]$, or tetrameric clusters as in the case of $[\{InMe(OH)(O_2PPh_2)\}_4(py)_4]$[13]. Synthesis of molecular gallium phosphonates involving a bulkier substituent (*tert*-butyl group) appeared in the literature[14,15]. It was shown by Mason *et. al.*[14], that, owing to bulkiness of *tert*-butyl group on gallium, it was possible to isolate and structurally characterize cyclic gallium phosphonate. Efforts have also been made to synthesize indium phosphonates with open structure[16,17]. In pursuance of our interest in the chemistry of Group 13 elements with phosphorous based acids, we have synthesized and characterized a series of diphenylphosphinate and di-n/t-butylphosphates of gallium(III) and indium(III).

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RESULTS AND DISCUSSION

Treatment of $GaCl_3$ or $InCl_3$ with sodium salt of diphenylphosphinic acid in 1:3 stoichiometry in benzene yields tris-diphenylphosphinates $[M(O_2PPh_2)_3]$ [M= Ga (**1**) or In (**2**)] as an insoluble white solid (eqn. 1). Reaction of MCl_3 with $[(Bu^nO)_2PO_2H]$ in the presence of triethylamine affords $[M\{O_2P(OBu^n)_2\}_3]$ [M= Ga (**4**) and In (**5**)] (eqn. 2). The solubility of the tris complex, $[Ga\{O_2P(OBu^t)_2\}_3]$ (**9**) in organic solvents, enabled us to synthesize it by the reaction of gallium trichloride with $K[O_2P(OBu^t)_2]$ (eqn. 3). A few chloro gallium complexes $[GaCl_{3\text{-}N}(O_2PR_2)_N]$ (N = 1 or 2) (eg. **3**) have been prepared either by redistribution reaction (eqn. 4) or by substitution of chloride in $GaCl_3$ with potassium or lead salts of the acid (eqn. 5) (eg. **6**,**7**,**8**). Attempts to prepare $[GaCl(O_2PPh_2)_2]$ by redistribution reaction leads to the formation of $[GaCl_2(O_2PPh_2)]$ and **1** (eqn. 6). Attempts to isolate $[GaCl_2\{O_2P(OBu^t)_2\}]$ employing reaction 5 leads to excessive decomposition.

$$MCl_3 + 3NaO_2PPh_2 \longrightarrow [M(O_2PPh_2)_3] + 3NaCl \qquad \ldots(1)$$
$$[M = Ga(1); In(2)]$$

$$MCl_3 + 3(Bu^nO)_2POOH + 3Et_3N \longrightarrow [M\{O_2P(OBu^n)_2\}_3] + 3Et_3N.HCl$$
$$[M = Ga(4); In(5)] \qquad \ldots(2)$$

$$\mathrm{GaCl_3 + 3K[O_2P(OBu^t)_2] \longrightarrow \underset{(9)}{[Ga\{O_2P(OBu^t)_2\}_3]} + 3KCl} \quad .(3)$$

$$\mathrm{2GaCl_3 + Ga(O_2PPh_2)_3 \longrightarrow 3\underset{(3)}{[GaCl_2(O_2PPh_2)]}} \quad \ldots(4)$$

$$\mathrm{GaCl_3{+}1/2N[Pb\{O_2P(OBu^n)_2\}_2]/N[KO_2P(OBu^t)_2]}$$
$$\mathrm{\longrightarrow [GaCl_{3-N}\{O_2P(OBu^x)_2\}_N]} \quad \ldots(5)$$
$$(\mathrm{x = n\ or\ t})$$

$$\mathrm{2Ga(O_2PPh_2)_3 + GaCl_3 \longrightarrow 3[GaCl(O_2PPh_2)_2] \longrightarrow 3/2(1) + 3/2(3)} \quad \ldots(6)$$

The tris diphenylphosphinate complexes **1** and **2** are white solids insoluble in all common organic solvents whereas the dichloro complex **3** is a white crystalline solid. The ν P-O were assigned by comparison with the IR spectra of diphenylphosphinic acid and its compounds[12,18–20]. The tris and dichloro complexes showed ν P-O in the region 1169–1058 $\mathrm{cm^{-1}}$. In the case of di-n-butylphosphate complexes **4, 5, 6** and **7**, strong broad bands were observed in the region 1200–1035 $\mathrm{cm^{-1}}$ in the IR spectra which were assigned to νP-O and νP=O stretchings. For the di-t-butylphosphate complexes **8** and **9**, the spectra showed νP=O at 1254 ± 2 $\mathrm{cm^{-1}}$ and νP-O at 1043 $\mathrm{cm^{-1}}$. The presence of a number of bands in the region 600–250 $\mathrm{cm^{-1}}$due to the alkyl/phenyl groups in all the complexes **1** to **9**, thwarted unambiguous identification of νGa-Cl, νGa-O and ν In-O bands.

The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of **3** in $\mathrm{CDCl_3}$solution exhibited a single resonance and appeared at higher frequency compared to the resonance of diphenylphosphinic acid (Table I). Attempts to prepare a monochloro complex $\mathrm{[GaCl(O_2PPh_2)_2]}$, by a redistribution reaction (eqn. 6) results in disproportionation. Thus the reaction of $\mathrm{GaCl_3}$ with **1** in $\mathrm{CDCl_3}$ was monitored by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy. Initially a nearly clear solution formed which showed three sharp resonances (δ 35.3, δ 26.9 and δ 18.7 ppm). This solution after a few hours became turbid and displayed a resonance assignable to **3**. The white precipitate isolated from this was identified as the tris complex **1** (see experimental). The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of dibutylphosphate chloro complexes **6, 7** and **9** showed single resonances which appeared at higher field compared to the free ligands or potassium salt. The solid state $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of tris complexes, **1**,

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2, **4** and **5** were recorded because of their insolubility in common organic solvents. The spectra exhibited single resonances which are shielded relative to the corresponding resonance for the acids. The shielding was more pronounced in gallium complexes than that of the corresponding indium derivatives. Similarly shielding of $^{31}P\{^{1}H\}$ NMR signal for **8** was observed.

The ^{1}H and ^{13}C NMR spectra of these complexes show characteristic resonances due to the alkoxy/phenyl protons/carbons at room temperature (Table I). The $^{13}C\{^{1}H\}$ resonances for the diphenylphosphinate group appeared as doublets due to $^{n}J(^{31}P\text{-}^{13}C)$ couplings. The magnitudes of these couplings are of the order of $^{1}J(^{31}P\text{-}^{13}C)$ ~135 Hz, $^{2}J(^{31}P\text{-}^{13}C)$ ~13 Hz, $^{3}J(^{31}P\text{-}^{13}C)$ ~10 Hz and $^{4}J(^{31}P\text{-}^{13}C)$ <3 Hz. As compared to diphenylphosphinic acid, the C-4 resonance in **3** showed broad peak instead of a doublet. For the di-n-butylphosphate complexes (*viz.* **6** and **7**), $J(^{31}P\text{-}^{13}C)$ couplings were observed for α and β carbons of n-butyl group in the free ligand and in the complexes.

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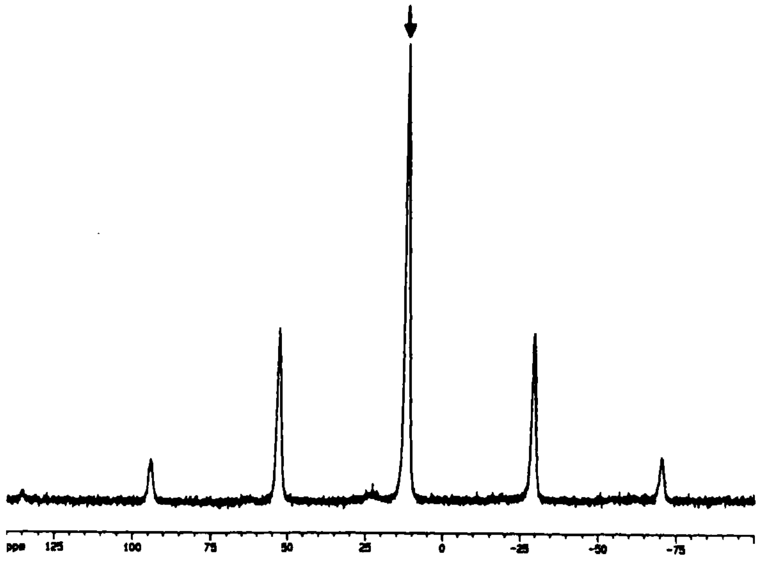

FIGURE 1 Solid state $^{31}P\{^{1}H\}$ NMR spectrum (spinning rate 5000 Hz) of 1. ↓ indicates central band

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TABLE I ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR and IR spectral data for gallium and indium complexes

Complex	*$^{31}P\{^1H\}$ NMR δ*		*$^{13}C\{^1H\}$ NMR δ*	*^1H NMR in $CDCl_3$ δ*	*IR absorptions in the region 600–300 cm^{-1}*
	Solution in $CDCl_3$	*Solid*			
$Ph_2P(O)OH$	33.2	27.6	128.2 (d, 13.5 Hz) C 3,5; 131.3 (d, 10.3 Hz) C-2,6; 131.7 (d, 2.7 Hz) C-4; 133.1 (d, 140 Hz) C-1.	6.90 (br)/OH; 7.28–7.39 (m), 7.60-7.70 (m) [Ph].	555, 526, 473, 435, 419, 398 375, 352, 335, 327, 315, 302.
$[Ga(O_2PPh_2)_3]$ (**1**)	_	11.9	_	_	568, 558, 533, 461, 421, 404. 389, 319, 303.
$[In(O_2PPh_2)_3]$ (**2**)	_	21.5	_	_	561, 527, 436, 358, 333, 309.
$[GaCl_2(O_2PPh_2)]$ (**3**)	35.3	_	128.9 (d, 14.4 Hz) C-3,5; 131.5 (d, 11.9 Hz) C-2,6; 131.3 (d, 152 Hz) C-1; 133.4 (br) C-4.	7.42–7.48 (m), 7.55–7.61 (m), 7.69–7.77 (m) (2:1:2) [Ph].	599, 551, 534, 464, 444, 414, 374, 323, 306.
$[(Bu^nO)_2POOH]$	1.2	_	13.4 (s, $OCH_2CH_2CH_2\underline{Me}$); 18.7 (s,$OCH_2CH_2\underline{C}H_2$); 32.3 (d,7 Hz, $OCH_2\underline{C}H_2$); 67.4 (d,5.6 Hz,OCH_2).	0.91(t,7.3Hz,$OCH_2CH_2CH_2\underline{Me}$); 1.39 (m,$OCH_2CH_2C\underline{H}_2$); 1.63 (m,$OCH_2C\underline{H}_2$); 4.01 (q, 6.8 Hz $OC\underline{H}_2$); 11.56 (br, OH).	518, 472, 419, 398, 375, 352, 327, 303.
$[Pb\{O_2P(OBu^n)_2\}_2]$	–0.3	----	13.7 (s, $OCH_2CH_2CH_2Me$); 19.0 (s, $OCH_2CH_2\underline{C}H_2$); 32.8 (d, 7.8 Hz, $OCH_2\underline{C}H_2$); 66.2 (d, 5.6 Hz, $O\underline{C}H_2$).	0.92 (t, 7.3 Hz,$OCH_2CH_2CH_2\underline{Me}$); 1.40 (sextet,5 Hz,$OCH_2CH_2C\underline{H}_2$): 1.62 (pentate, 7.4 Hz,$OCH_2C\underline{H}_2$); 3.95 (quartet, 6.3 Hz, $OC\underline{H}_2$).	559. 535, 475, 451, 429, 385, 304.
$[Ga\{O_2P(OBu^n)_2\}_3]$ (**4**)	_	–12.3	_	_	558, 518, 472, 315, 302.

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Complex	*$^{31}P\{^1H\}$ NMR δ*		*$^{13}C\{^1H\}$ NMR δ*	*^1H NMR in $CDCl_3$ δ*	*IR absorptions in the region 600–300 cm^{-1}*
	Solution in $CDCl_3$	*Solid*			
$[In\{O_2P(OBu^n)_2\}_3]$ (5)		−8.1	----	----	559, 526, 473, 419, 397, 352. 325, 303.
$[GaCl\{O_2P(OBu^n)_2\}_2]$ (6)	−7.0	–	13.5 (s, $-OCH_2CH_2CH_2\underline{Me}$); 18.7 (s, $-OCH_2CH_2\underline{C}H_2$); 32.3 (d, 6.2 Hz,- $OCH_2\underline{C}H_2$); 68.4 (br, $-O\underline{C}H_2$)	0.90 (dt, $-OCH_2CH_2CH_2\underline{Me}$); 1.35 (m, $-OCH_2CH_2C\underline{H}_2$); 1.65 (m, $-OCH_2C\underline{H}_2$); 3.95 (br, $-OC\underline{H}_2$)	522(br). 474, 391, 361. 303.
$[GaCl_2\{O_2P(OBu^n)_2\}]$ (7)	−10.0	----	13.4 (s,$-OCH_2CH_2CH_2\underline{Me}$):18.6 (s,$-OCH_2CH_2\underline{C}H_2$); 32.0 (d, 7.15 Hz,- $OCH_2\underline{C}H_2$); 69.8 (br,$-O\underline{C}H_2$)	0.95 (t,7.4Hz,$-OCH_2CH_2CH_2\underline{Me}$); 1.45 (m, $-OCH_2CH_2C\underline{H}_2$); 1.71 (m,$-OCH_2C\underline{H}_2$); 4.15 (q, 6 Hz. $OC\underline{H}_2$).	526, 472, 399, 359.
$K\{O_2P(OBu^t)_2\}$[a]	−6.4	–	30.1 (s, $OC\underline{Me}_3$); 78.8 (d, 6.9 Hz, $O\underline{C}Me_3$)	1.37 (s, $OC\underline{Me}_3$)	584, 546, 495, 461, 398, 353, 326, 307.
$[Ga\{O_2P(OBu^t)_2\}_3]$ (8)	−7.1	–	30.0 (d, 3.3Hz, $-OC\underline{Me}_3$); 81.1 (br, $O\underline{C}Me_3$)	1.48 (s, $OC\underline{Me}_3$)	419, 398, 375, 352, 335, 327, 303.
$[GaCl\{O_2P(OBu^t)_2\}_2]$[b] (9)	−8.4	–	30.1 ($OC\underline{Me}_3$): 82.0 (br,$O\underline{C}Me_3$)	1.47 (s,$-OC\underline{Me}_3$)	485, 397, 375, 357, 342, 303.

a. in D_2O.
b. in acetone-d_6.

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TABLE II Yield and analytical data for Ga(III)/In(III) diphenylphosphinic and dibutylphosphate complexes

Reactants (g, mmol)			*Product (yield in g, %)*	*M.P. (°C)*	*% Analysis Found (calcd.)*		
					C	*H*	*Ga/In*
$GaCl_3$ (0.69, 3.92)	+	Ph_2POONa (2.85, 11.87)	$[Ga(O_2PPh_2)_3]$ (**1**) (2.14, 75)	>240	59.7 (59.9)	4.1 (4.2)	9.6 (9.7)
$InCl_3$ (0.61, 2.76)	+	Ph_2POONa (1.97, 8.20)	$[In(O_2PPh_2)_3]$ (**2**) (1.82, 87)	>225	55.5 (56.4)	3.9 (3.9)	14.9 (15.0)
$GaCl_3$ (0.16, 0.88)	+	$[Ga(O_2PPh_2)_3]$ (0.32, 0.44)	$[GaCl_2(O_2PPh_2)]$ (**3**) (0.47, 98)	135 – 137	39.9 (40.2)	2.8 (2.8)	19.5 (19.5)
$GaCl_3 + Et_3N + (Bu^nO)_2POOH$ (0.53, 3.01) (0.92, 9.09) (1.91, 9.09)			$[Ga\{O_2P(OBu^n)_2\}_3]$ (**4**) (1.73, 82)	>225	40.6 (41.3)	7.6 (7.8)	9.9 (10.0)
$InCl_3 + Et_3N + (Bu^nO)_2POOH$ (0.63, 2.85) (0.87, 8.60) (1.81, 8.62)			$[In\{O_2P(OBu^n)_2\}_3]$ (**5**) (1.69, 79)	>225	38.6 (38.8)	6.9 (7.3)	15.3 (15.5)
$GaCl_3$ (0.55, 3.12)	+	$\{(Bu^nO)_2POO\}_2Pb$ (1.96, 3.13)	$[GaCl\{O_2P(OBu^n)_2\}_2]$ (**6**) (1.01, 62)	liquid	------	-----	13.2 (13.3)
$GaCl_3$ (0.49, 2.78)	+	$\{(Bu^nO)_2POO\}_2Pb$ (0.89, 1.42)	$[GaCl_2\{O_2P(OBu^n)_2\}]$ (**7**) (0.98, 99)	liquid	------	-----	19.9 (19.9)
$GaCl_3$ (0.49, 2.78)	+	$(Bu^tO)_2POOK$ (2.09, 8.42)	$[Ga\{O_2P(OBu^t)_2\}_3]$ (**8**) (1.01, 52)	liquid	-----	-----	9.8 (10.0)
$GaCl_3$ (0.62, 3.52)	+	$(Bu^tO)_2POOK$ (1.75, 7.05)	$[GaCl\{O_2P(OBu^t)_2\}_2]$ (**9**) (1.74, 94)	a			13.2 (13.3)

a. Gas evolution occured in the temperature range 60–80°C.

In order to isolate mixed ligand complexes, a few reactions of **3** with some thio ligands were investigated. Reactions of **3** with ammonium diethyldithiophosphate $NH_4[S_2P(OEt)_2]$ gave disproportionation products $[Ga\{S_2P(OEt)_2\}_3]$ and **1** (insoluble). Reaction of sodium salt of 2-mercaptoethylether with $GaCl_3$, followed by treatment with sodium diphenylphosphinate gave $[Ga(O_2PPh_2)\{SCH_2CH_2)_2O\}]$.

Extensive work on groups IV and V complexes of phosphorous based acids has revealed that these ligands bind the metal atom in several different ways[3]. The gallium and indium complexes with dithio acid ligands, *e.g.* xanthates[21a], dithiocarbamates[21b] and dithiophosphates[8,9], are discrete mononuclear species with chelating ligands. X-ray structural studies on organometallic complexes of gallium and indium with $[PO_3]^-$ [11–15] have revealed their associated structures. It can be tentatively inferred from the above discussion that the tris complexes (**1**, **2**, **4** and **5**) are associated molecules while complex **8** may be a tris chelate. The high solubility of the chloro complexes (**3**, **6**, **7**, **9**) in organic solvents and the presence of single set of resonances in NMR spectra suggest that they may be monomeric in solution with chelating ligands.

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EXPERIMENTAL

All experiments using organic solvents were performed under anhydrous conditions in a nitrogen atmosphere using Schlenck techniques. Pertinent data of these compounds are given in Table II. High purity (99.999%) $GaCl_3$ and $InCl_3$were used as received from Trans Metal. Diphenylphosphinic acid $[Ph_2P(O)OH]$ was prepared by oxidation of Ph_2PCl (Aldrich) with a mixture of HNO_3/H_2O_2 and then recrystallized from ethanol as white prismatic crystalline solid (m.p. 91°C)[22]. Potassium di-tert-butylphosphate $K[O_2P(OBu^t)_2]$ was prepared according to literature method[23,24]. Di-n-butylphosphate was obtained from Fluka. Infrared spectra were recorded either as neat liquids or as Nujol mulls between CsI plates on a Bomem MB-102 FT IR spectrometer. The NMR spectra (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) were recorded on a Bruker DPX-300 NMR spectrometer in 5mm tube in $CDCl_3$ solutions using freshly prepared samples. The chemical shifts were referenced to the internal chloroform peak (δ 7.26 and δ 77.0 ppm) for ^1H and $^{13}C\{^1H\}$ NMR respectively and external

85% H_3PO_4 for $^{31}P\{^1H\}$. The solid state $^{31}P\{^1H\}$ NMR spectra were recorded in 7 mm zircona rotor with a CP Mass probe head with at least three different spinning rates and were referenced with sodium dihydrogen phosphate.

Preparation of [$Ga(O_2PPh_2)_3$] (1)

A methanolic solution (20 ml) of Ph_2PO_2H (2.589g, 11.87 mmol) was added to sodium methoxide (prepared from 273 mg Na in 20 ml methanol). Reactants were stirred at RT for 2 h. The solvent was evaporated *in vacuo* to leave a white solid [NaO_2PPh_2]. The sodium salt was suspended in benzene (50 ml) and a benzene solution (20 ml) of $GaCl_3$ (696 mg, 3.95 mmol) was added with stirring which was continued for 4h. The white solid was filtered, washed several times with dry methanol until the washings were free from sodium chloride. The white solid was then dried in vacuum (yield 2.14 g, 75%).

Similarly [$In(O_2PPh_2)_3$] (2) was prepared in 87% yield.

Attempted preparation of [$GaCl(O_2PPh_2)_2$]

To a benzene suspension (20 ml) of [$Ga(O_2PPh_2)_3$] (3.87 g, 5.37 mmol), a solution of $GaCl_3$ (470 mg, 2.68 mmol) in benzene was added and stirred under nitrogen for 3h. Initially a clear solution was formed from which a white solid precipitated out gradually (completes in 50 hrs). This was filtered to give a white solid (3.28 g, Analysis-Found: C,59.8; H,4.0; Ga, 9.6%; Calcd. for $C_{36}H_{30}O_6P_3Ga$: C,59.9; H,4.2; Ga, 9.7%) and was characterized as [$Ga(O_2PPh_2)_3$]. The filtrate on evaporation under reduced pressure gave a white solid (430 mg) m.p. 135–137°C. Analysis- Found: C, 39.9; H, 2.6; Ga, 19.5%; Calcd. for $C_{12}H_{10}Cl_2O_2PGa$: C, 40.2; H, 2.8; Ga, 19.5%) and was identified as [$GaCl_2(O_2PPh_2)$].

Preparation of [$GaCl_2(O_2PPh_2)$] (3)

To a benzene solution (20 ml) of $GaCl_3$ (160 mg, 0.88 mmol), [$Ga(O_2PPh_2)_3$] (320 mg, 0.44 mmol) suspension (50 ml) in benzene/dichloromethane was added and stirred for 4 hr under nitrogen, whereupon a clear solution formed. The solvents were evaporated *in vacuo*

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to give a white solid (470 mg, 98% yield). It was recrystallized from $CDCl_3$/toluene mixture to yield white crystals which turned powdery on removing the solvent.

Preparation of $[Ga\{O_2P(OBu^n)_2\}_3]$ (4)

To a benzene solution of Et_3N (920 mg, 9.09 mmol) and $GaCl_3$ (530 mg, 3.03 mmol), $(Bu^nO)_2PO_2H$ (1.91 g, 9.09 mmol) solution in benzene was added dropwise with vigorous stirring. The mixture was stirred for 2 h and then filtered through a G-3 filtration unit using a suction pump. The residue was washed repeatedly with dichloromethane to remove $Et_3N.HCl$. until the filtrate gave a negative test for the presence of chloride ion. The white solid residue in the filtering funnel was dried (yield 1.73 g, 82%).

$[In\{O_2P(OBu^n)_2\}_3]$ (5) was prepared (79% yield) using a similar method.

Preparation of $[GaCl_2\{O_2P(OBu^n)_2\}]$ (7)

To a benzene solution of $[\{(Bu^nO)_2PO_2\}_2Pb]$ (899 mg, 1.41 mmol), a benzene solution of $GaCl_3$ (490 mg, 2.82 mmol) was added in a Schlenck tube. The mixture was stirred for 3h and then filtered to remove $PbCl_2$. The benzene was evaporated from the clear filtrate under reduced pressure to give an oily residue.

Similar method was used to prepare $[GaCl\{O_2P(OBu^n)_2\}_2]$ (6).

Preparation of $[Ga\{O_2P(OBu^t)_2\}_3]$ (8)

To a benzene suspension of $K[O_2P(OBu^t)_2]$ (2.09 g, 8.45 mmol), a benzene solution of $GaCl_3$ (0.49 gm, 2.82 mmol) was added and stirred under nitrogen for 3h. It was filtered through a G-3 filtration unit using a suction pump. The clear filtrate was evporated *in vacuo* to give an oily liquid which was characterized immediately (decomposes on keeping for some time at room temperature).

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Preparation of $[GaCl\{O_2P(OBu^t)_2\}_2]$ (9)

To a benzene solution of $GaCl_3$ (620 mg, 3.52 mmol), a benzene suspension of $K[O_2P(OBu^t)_2]$ (1.75 g, 7.05mmol) was added and stirred for 3h under nitrogen. It was filtered through a G-3 filtration unit using a suction pump and the filtrate was evaporated under reduced pressure. A solid was obtained which being prone to decomposition was characterized immediately.

Reaction between 3 and $NH_4[S_2P(OEt)_2]$

To a benzene solution (20 ml) of **3** (476 mg, 1.33 mmol), solid $NH_4[S_2P(OEt)_2]$ (543 mg, 2.66 mmol) was added and the solution was stirred for 4 hr at room temperature. It was filtered through a G-3 filtration unit using suction pump. The filtrate on concentration gave $[Ga\{S_2P(OEt)_2\}_3]$ [^1H NMR: δ 1.30 (t, 7Hz, OCH_2Me); δ 4.19 (dq, 7Hz, (q); 9.9 Hz (d) OCH_2-), ^{31}P NMR: δ 91.4 ppm]. NH_4Cl was removed from the residue by dissolving in excess dry methanol. The white insoluble solid was characterized as $[Ga(O_2PPh_2)_3]$. [Analysis- Found: C, 59.6; H, 4.1; Ga, 9.5% Calcd. for $C_{36}H_{30}O_6P_3Ga$; C, 59.8, H, 4.2; Ga, 9.7%].

Reaction between $[(NaSCH_2CH_2)_2O]$, $GaCl_3$ and Ph_2PO_2Na

$[GaCl\{(SCH_2CH_2)_2O\}]$, prepared by stirring a benzene solution of $GaCl_3$ (912 mg, 5.18 mmol) and $[(NaSCH_2CH_2)_2O]$ [$(HSCH_2CH_2)_2O$ (716 mg, 5.18 mmol) and sodium (238 mg) in methanol and then dried in vacuo)] for 3 hrs, was treated with NaO_2PPh_2 [prepared from $Ph_2P(O)OH$ (1.129g, 5.18 mmol) and sodium (119 mg) in methanol. The whole was stirred at room temperature for 3 hrs. Precipitated sodium chloride was filtered off and the filtrate was concentrated in vacuo to give a white solid (2.2 g, 99% yield). It was recrystallized from CH_2Cl_2 to yield white crystals which turned powdery on removing the solvent. Analysis-Found: C,44.9; H,4.3; Ga,16.4%. Calcd. for $C_{16}H_{18}GaO_3PS_2$: C, 45.2; H,4.3; Ga,16.4%. ^{31}P NMR: δ 23.9 ppm.

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