DE GRUYTER Main Group Met. Chem. 2014; 37(5-6): 163–167

Short Communication

Syed Usman Ahmad, Andrew Duthie and Jens Beckmann*

Synthesis and structure of three molecular arylindium phosphinates

Abstract: Reported here are the syntheses and molecular structures of three novel arylindium phosphinates, $[(2,6\text{-Mes}_2C_6H_3In)_2(OH)_2(O_2PMe_2)_2]$ (**1**), $[(2,6\text{-Mes}_2C_6H_3In)_2(OH)(O_2PPh_2)_3]$ (**2**), and $[(2,6\text{-Mes}_2C_6H_3In)(O_2PMe_5C_3H)_2(H_2O)_2]$ (**3**), which were obtained by condensation reaction of the *m*-terphenylindium dihydroxide $[(2,6\text{-Mes}_2C_6H_3In(OH)_2]_4$ with dimethylphosphinic acid, diphenylphosphinic acid, and 2,2,3,4,4-pentamethylphosphetanic acid, respectively.

Keywords: indium; phosphinates; structure determination.

DOI 10.1515/mgmc-2014-0023
Received July 4, 2014; accepted August 14, 2014; previously

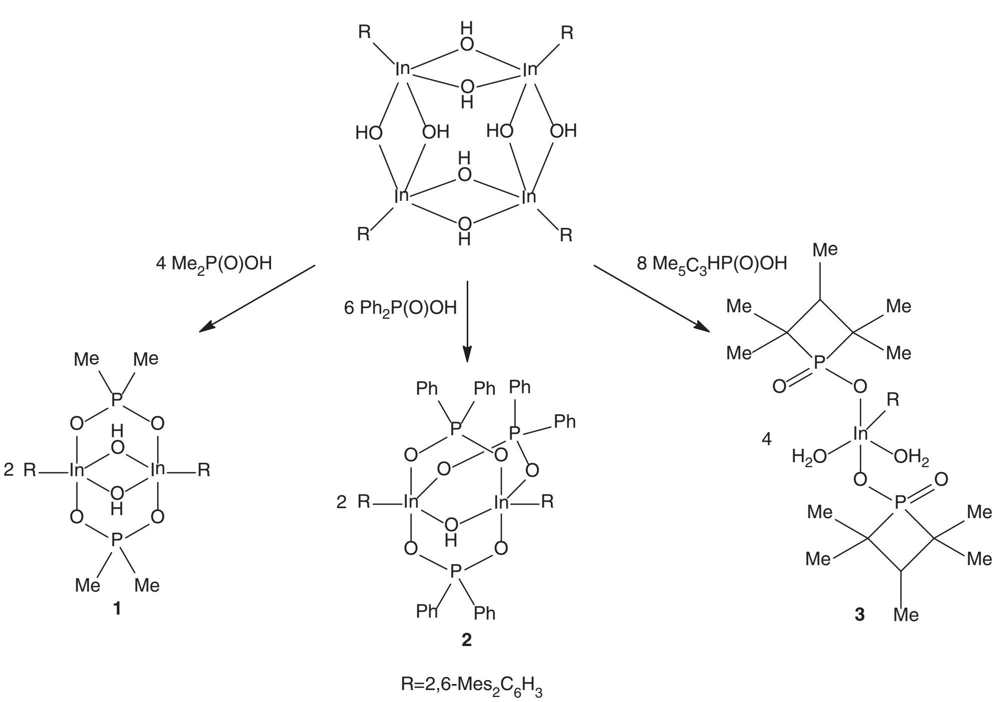
The chemistry of group 13 element phosphinates dating back to the pioneering work of Coates and Mukherjee (1964) was comprehensively reviewed more than 15 years ago (Mason, 1998). Unarguably, aluminium phoshinates have received the most attention due to the fact that the Al-O-P linkage is isoelectronic to the Si-O-Si linkage and implications that hold for applications in material science. Among the very few known indium phosphinates, the most notable are the eight-membered heterocycles $(R'_2InO_2PR_2)_2$ (R′=Me, Et; R=Me, Ph), which were obtained by the reaction of the phosphinic acids R_2PO_2H with the indium trialkyls R_3In or the oxidation of $(Me_2InPPh_2)_2$ with pyridine oxide (Coates and Mukherjee, 1964; Hahn et al., 1990). The hydrolysis of $(Me_2InO_2PPh_2)_2$ in the presence of pyridine (py) gave the unique tetrameric heterocubane cluster $[MeIn(OH)(O_2PPh_2]_4\cdot 4$ py (Arif and Barron, 1988). Recently, we reported on the tetranuclear *m*-terphenylindium dihydroxide $[2,6\text{-Mes}_2C_6H_3In(OH)_2]_4$, which can be regarded as a heavier congener of the common arylboronic acids (Ahmad and Beckmann, 2009). We now describe the reactions of $[2,6\text{-Mes}_2C_6H_3In(OH)_2]_4$ with dimethylphosphinic acid, diphenylphosphinc acid, and 2,2,3,4,4-pentamethylphosphetanic acid, respectively, which gave rise to the formation of the arylindium phosphinates $[(2,6\text{-Mes}_2C_6H_3In)_2(OH)_2(O_2PMe_2)_2]$ (**1**), $[(2,6\text{-Mes}_2C_6H_3In)_2(OH)(O_2PPh_2)_3]$ (**2**), and $[(2,6\text{-Mes}_2C_6H_3In)(O_2PMe_5C_3H)_2(H_2O)_2]$ (**3**) as sole products regardless of the stoichiometric ratio of the reactants applied (Scheme 1).

Compounds **1**–**3** were obtained as colorless high-melting crystalline solids that are reasonably soluble in quite polar solvents, such as $CHCl_3$, CH_2Cl_2, and THF. The In/P ratios of **1** (1:1), **2** (2:3), and **3** (1:2) were determined by integration of ^1H NMR resonances (see Experimental) and confirmed by elemental analysis. The ^{31}P NMR spectra ($CDCl_3$) and ^{31}P MAS NMR spectra of **1**–**3** reveal signals at δ=40.5 and δ_{iso}=44.1 for **1**, δ=31.8, 28.0 (integral ratio 1:2) and δ_{iso}=28.8, 23.6 (integral ratio 1:2) for **2**, and δ=49.4 and δ_{iso}=49.7 for **3**, which shifted significantly upfield from those of the parent phosphinic acids $Me_2P(O)OH$ (δ=54.1), $Ph_2P(O)OH$ (δ=38.7), and $Me_5C_3HP(O)OH$ (δ=60.2), respectively. The molecular structures of **1**–**3** established by single crystal X-ray diffraction are depicted in Figures 1–3, respectively, and selected bond parameters are collected in the caption of the figures.

The degree of aggregation of the indium phosphinates **1**–**3** is smaller than in the tetranuclear starting material. While **1** and **2** are dinuclear, **3** is even mononuclear presumably due to the fact that 1,1,2,3,3-pentamethyltrimethylenephosphinate (Chandrasekhar et al., 2004; Chandrasekhar and Thirumoorthi, 2009) is bulkier than the dimethyl- and diphenylphosphinate.

In the crystal structure of **1**, the two In atoms are bridged via two μ-OH groups and two μ-O_2PMe_2 groups. In the crystal structure of **2**, the two In atoms are bridged via one μ-OH group and three μ-O_2PPh_2 groups. The spatial arrangement of the In atoms is trigonal bipyramidal and defined by a CO_4 donor set.

***Corresponding author: Jens Beckmann,** Institut für Anorganische Chemie, Universität Bremen, Leobener Straße, D-28359 Bremen, Germany, e-mail: j.beckmann@uni-bremen.de; and Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, D-14195 Berlin, Germany
Syed Usman Ahmad: Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, D-14195 Berlin, Germany
Andrew Duthie: School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia



Scheme 1 Synthesis of the arylindium phosphinates **1–3**.

The In-O bond, lengths vary between 2.104(8) and 2.247(4) Å and compare well with those of the starting compound [(2,6-$Mes_2C_6H_3In(OH)_2]_4$ (Ahmad and Beckmann, 2009), the previously reported indium phosphinates (Arif and Barron, 1988; Hahn et al., 1990), and the recently published indium phosphonates

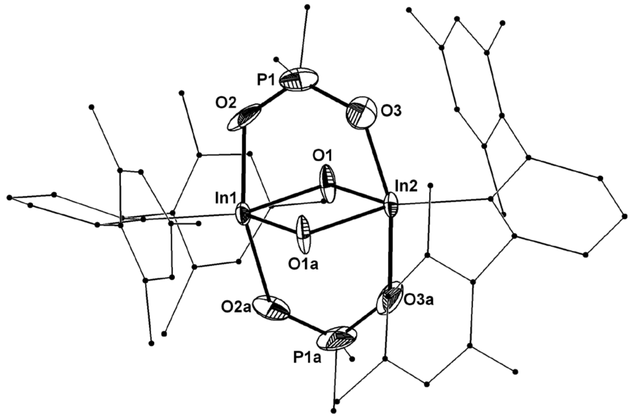


Figure 1 Molecular structure of **1** showing 30% probability ellipsoids and the crystallographic numbering scheme.
Selected bond lengths [Å]: In1-O1 2.104(8), In1-O1a 2.104(8), In1-O2 2.16(1), In1-O2a 2.16(1), In1-C30 2.134(3), In2-O1 2.145(7), In2-O1a 2.145(7), In2-O3 2.14(1), In2-O3a 2.14(1), In2 -C10 2.14(2), P1-O2 1.51(2), P1-O3 1.49(2), P1-C1 1.75(2), P1-C2 1.79(2).

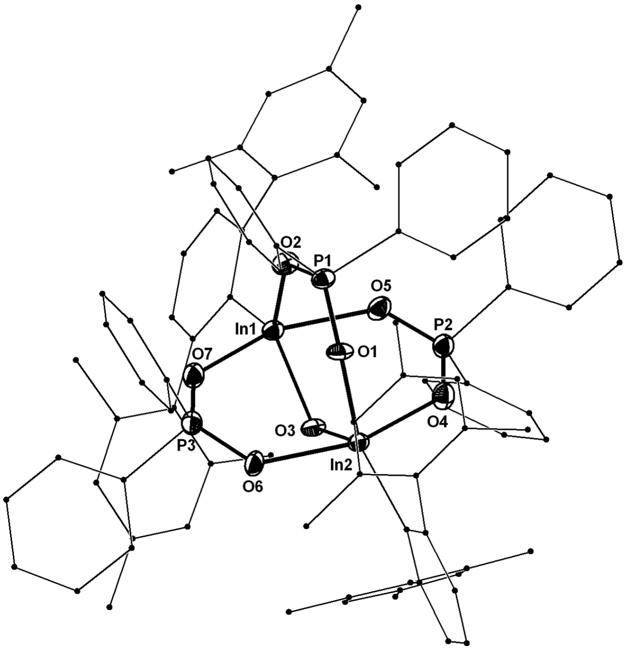


Figure 2 Molecular structure of **2** showing 30% probability ellipsoids and the crystallographic numbering scheme.
Selected bond lengths [Å]: In1-O2 2.121(4), In1-O3 2.140(3), In1-O5 2.207(4), In1-O7 2.247(4), In1-C80 2.137(6), In2-O1 2.118(3), In2-O3 2.121(4), In2-O4 2.197(4), In2-O6 2.232(4), In2-C120 2.167(5), P1-O1 1.521(3), P1-O2 1.499(4), P1-C10 1.800(6), P1-C20 1.793(5), P2-O4 1.510(4), P2-O5 1.514(4), P2-C40 1.795(7), P2-C50 1.805(6), P3-O6 1.521(4), P3-O7 1.500(4), P3-C60 1.801(7), P3-C70 1.798(6).

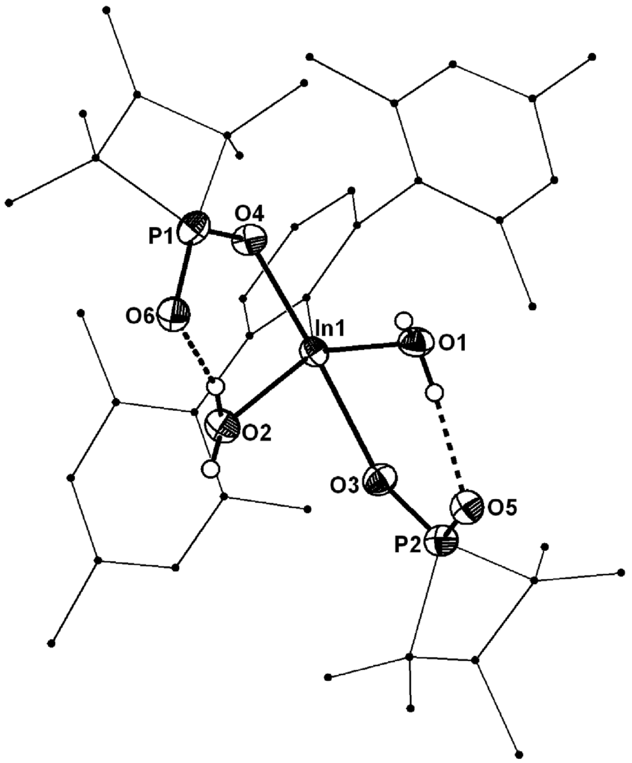


Figure 3 Molecular structure of **3** showing 30% probability ellipsoids and the crystallographic numbering scheme.
Selected bond lengths [Å]: In1-O1 2.121(5), In1-O2 2.126(5), In1-O3 2.225(4), In1-O4 2.240(4), In1-C10 2.141(6), P1-O4 1.508(4), P1-O6 1.529(5), P1-C80 1.831(7), P1-C82 1.842(7), P2-O3 1.509(4), P2-O5 1.511(5), P2-C70 1.858(7), P2-C72 1.834(8), In2-O7 2.134(5), In2-O8 2.129(5), In2-O9 2.215(5), In2-O10 2.237(5), In2-C40 2.125(6), P3-O9 1.514(5), P3-O11 1.517(4), P3-C100 1.847(8), P3-C102 1.804(8), P4-O10 1.480(5), P4-O12 1.513(4), P4-C90 1.816(8), P4-C92 1.832(8), O1···O5 2.647(6), O2···O6 2.659(7).

(Chandrasekhar et al., 2013). The structures of **1** and **2** contain μ-OH groups, whereas that of **3** possesses two H_2O molecules that coordinate to the In atom and engage in hydrogen bonding with the P=O groups of the phosphinate moieties [O···O 2.647(6) and 2.659(7) Å]. Consistently, the IR spectra (KBr) show absorptions at $\tilde{\nu}$=3624 cm^{-1} for **1**, $\tilde{\nu}$=3587 cm^{-1} for **2**, and $\tilde{\nu}$=3626 cm^{-1} for **3** that are indicative of O-H stretching vibrations.

Experimental

General

The *m*-terphenylindium dihydroxide $[(2,6\text{-}Mes_2C_6H_3In(OH)_2]_4$ (Ahmad and Beckmann, 2009) and the 2,2,3,4,4-pentamethylphosphetanic acid $Me_5C_3HP(O)OH$ (Emsley et al., 1984) were prepared according to literature procedures. The other two phosphinic acids $Me_2P(O)OH$ and $Ph_2P(O)OH$ were obtained commercially and used as received. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^1H, ^{13}C) and aqueous H_3PO_4 (^{31}P). The ^{31}P MAS NMR spectra were obtained using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6-mm rotor operating at spinning frequencies between 8 and 10 kHz. Infrared (IR) spectra were recorded using a Nexus FTIR spectrometer with a Smart DuraSamplIR. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of $[(2,6\text{-}Mes_2C_6H_3In)_2(OH)_2(O_2PMe_2)_2]$ (1)

A mixture of $[2,6\text{-}Mes_2C_6H_3In(OH)_2]_4$ (200 mg, 0.11 mmol) and $Me_2P(O)OH$ (40 mg, 0.40 mmol) in THF (25 mL) was stirred overnight at r.t. The solvent was completely removed in vacuum and the solid residue recrystallized from THF to give **1** (153 mg, 0.14 mmol, 64%; Mp. 290–292°C).

^1H-NMR: δ=7.36–7.32 (m, 2H), 7.02, 6.97 (d, 4H), 6.89, 6.87 (s, 8H), 2.54, 2.39 (s, 12H), 2.00, 1.98 (s, 24H), 0.90 (d, 12H). ^{13}C NMR: δ=148.5, 148.3, 142.8, 142.1, 137.9, 136.9, 136.2, 136.0, 135.5, 135.3, 128.4, 128.2, 128.0, 127.8, 127.3, 126.4, 21.8, 21.7, 21.4, 21.3, 21.2, 20.9, 18.3, 17.3. ^{31}P NMR: δ=40.5. ^{31}P MAS NMR: δ_{iso}=44.1. IR (KBr): $\tilde{\nu}$ (OH)=3624 cm^{-1}. Anal. calcd for $C_{52}H_{80}In_2O_6P_2$ (1092.74): C, 57.14; H, 7.32. Found: C, 57.15; H, 7.23.

Synthesis of $[(2,6\text{-}Mes_2C_6H_3In)_2(OH)(O_2PPh_2)_3]$ (2)

A mixture of $[2,6\text{-}Mes_2C_6H_3In(OH)_2]_4$ (190 mg, 0.10 mmol) and $Ph_2P(O)OH$ (140 mg, 0.64 mmol) in THF (25 mL) was stirred overnight at r.t. The solvent was completely removed in vacuum and the solid residue recrystallized from CH_2Cl_2/hexane (1:3) to give **2** (0.27 mg, 0.17 mmol, 87 %; Mp. 330°C [dec.]).

^1H-NMR: δ=7.41–7.35 (m, 5H), 7.30 (t, 1H), 7.25–7.18 (m, 5H), 7.13–7.05 (m, 4H), 6.93 (d, 2H), 6.74 (s, 4H) 2.18 (s, 6H), 2.09 (s, 12H). ^{13}C-NMR: δ=149.2, 147.7, 142.3, 142.2, 137.3, 136.8, 136.5, 135.9, 135.7, 131.7, 131.6, 130.9, 130.2, 130.1, 129.4, 128.5, 128.3, 128.1, 127.7, 127.6, 127.2, 127.1, 127.0, 125.7, 21.5, 21.4. ^{31}P NMR: δ=31.8 (s, 1P), 28.0 (s, 2P). ^{31}P MAS NMR: δ_{iso}=28.8 (s, 1P), 23.6 (s, 2P). IR (KBr): $\tilde{\nu}$ (OH)=3587 cm^{-1}. Anal. calcd for $C_{84}H_{80}In_2O_7P_3$ (1524.03): C, 66.14; H, 5.24. Found: C, 66.15; H, 5.19.

Synthesis of $[(2,6\text{-}Mes_2C_6H_3In)(Me_5C_3HPO_2)_2(H_2O)_2]$ (3)

A mixture of $[2,6\text{-}Mes_2C_6H_3In(OH)_2]_4$ (110 mg, 0.06 mmol) and $Me_5C_3HP(O)OH$ (100 mg, 0.47 mmol) in THF (25 mL) was stirred overnight at r.t. The solvent was completely removed in vacuum and the solid residue was recrystallized from CH_2Cl_2/hexane (1:3) to give **3** (167 mg, 0.20 mmol, 86 %; Mp. 263–265°C).

^1H NMR: δ=7.33 (t, 1H), 6.94 (d, 2H), 6.89 (s, 4H), 2.39 (s, 6H), 1.99 (s, 12H), 1.00–0.70 (m, 32H). ^{13}C NMR: δ=148.8, 142.0, 136.6, 135.8, 128.8, 128.5, 128.2, 126.6, 49.8, 49.0, 41.9, 24.2, 22.6, 21.2, 21.1, 19.1. ^{31}P NMR: δ=49.4. ^{31}P MAS NMR: δ_{iso}=49.7. IR (KBr): $\tilde{\nu}$ (OH)=3626 cm^{-1}.

Table 1 Crystal data and structure refinement of **1**–**3**.

	1	2	3
Formula	$C_{52}H_{80}In_2O_6P_2$	$C_{84}H_{80}In_2O_7P_3$	$C_{40}H_{62}InO_6P_2$
Formula weight, g mol^{-1}	1092.74	1524.03	815.66
Crystal system	Triclinic	Monoclinic	Monoclinic
Crystal size, mm	0.7×0.6×0.5	0.7×0.6×0.5	0.6×0.6×0.4
Space group	C2/c	$P2_1/c$	$P2_1/a$
a, Å	13.841(3)	14.746(8)	24.879(15)
b, Å	22.730(5)	23.594(19)	16.485(5)
c, Å	17.909(4)	20.913(17)	26.029(16)
α, °	90	90	90
β, °	111.72(3)	95.38(6)	116.12(4)
γ, °	90	90	90
V, Å^3	5234(2)	7244(9)	9585(9)
Z	4	4	8
ρ_{calcd}, Mg m^{-3}	1.387	1.397	1.130
μ (Mo-Kα), mm^{-1}	0.988	0.758	0.596
F(000)	2272	3132	3432
θ range, deg	1.76 to 25.25	1.81 to 29.24	2.66 to 29.26
Index ranges	$-16 \le h \le 15$	$-17 \le h \le 20$	$-28 \le h \le 34$
	$0 \le k \le 27$	$-27 \le k \le 32$	$-22 \le k \le 22$
	$0 \le l \le 21$	$-28 \le l \le 28$	$-35 \le l \le 35$
No. of reflns collected	4603	49527	67449
Completeness to θ_{max}	97.0%	98.5%	97.9%
No. indep. reflns	4603	19,461	25,594
No. obsd reflns with $(I>2\sigma(I))$	2530	7420	5543
No. refined params	279	865	0.542
GooF (F^2)	0.990	0.749	0.542
R_1 (*F*) $(I>2\sigma(I))$	0.0827	0.0542	0.0533
wR_2 (F^2) (all data)	0.2178	0.1127	0.1076
Largest diff peak/hole, e Å^{-3}	1.153 /-1.400	0.464 /-1.079	0.364 /-0.379
CCDC number	1007858	1007859	1007869

Anal. calcd for $C_{40}H_{62}InO_6P_2$ (815.66): C, 58.84; H, 7.60. Found: C, 58.67; H, 7.43.

X-ray crystallography

Intensity data were collected on a STOE IPDS 2T diffractometer at 150 K with graphite-monochromated Mo-Kα (0.7107 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 and SHELXL-97 implemented in the program WinGX 2002 (Farrugia, 1999). Full-matrix least-squares refinements on F^2 were performed using all data. All nonhydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically.

Disorder was resolved in for C12, C13, C32, and C33 of **1** as well as C71 of **3** and refined with occupancy ratios of 50:50. The crystal lattice of **3** contained larger voids, the defuse electron density of which was accounted by Platon's Squeeze routine (Van der Sluis and Spek, 1990; Spek, 2003). Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND (Brandenburg and Putz, 2006). Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgments: We are indebted to Prof. Dr. Vadapalli Chandrasekhar (IIT Kanpur, India) for a gift of 2,2,3,4,4-pentamethylphosphetanic acid. Dr. Malte Hesse (Universität Bremen) is thanked for the collection of the X-ray diffraction data. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

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