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(5-Benzylidibenzo[*b,d*]phosphole 5-oxide)-trimethylindium

WENJIE WANG,^a YI PAN,^{a*} XIAOYING HUANG,^b HONGSUI SUN,^a ZHIBING LU^a AND XIANGZHEN SUN^{a*}

^aState Key Laboratory of Coordination Chemistry, Department of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China, and ^bState Key Laboratory of Structural Chemistry, Fuzhou 250003, People's Republic of China

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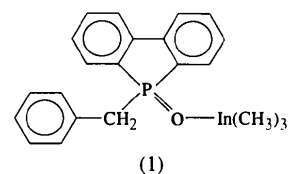
Abstract

The X-ray crystal structure determination of the title compound, [In(CH₃)₃(C₁₉H₁₅OP)], shows that the In atom has a four-coordinate distorted tetrahedral environment with an In—O bond length of 2.261 (3) Å. The In—O—P linkage is bent with a bond angle of 135.9 (2)°.

Comment

High-purity indium trialkyls have been used extensively in the growth of compound semiconductors by metal-organic chemical vapour deposition (MOCVD). One of the most successful purification methods for indium trialkyls may be called adduct purification, which involves the formation, purification and dissociation of non-volatile trialkylindium adducts. Donor ligands applied hitherto have mainly been N- and P-containing Lewis bases (Bradley, Chudzynska & Frigo, 1988; Bradley *et al.*, 1988; Foster, Rushworth, Cole-Hamilton, Jones & Stagg, 1988; Moore *et al.*, 1986). In the course of our work on searching for new useful adducts for the purification of indium trialkyls, we isolated the title

compound, (1). The X-ray structure of (1) is presented in Fig. 1.



In contrast to indium halide phosphine oxide complexes, in which indium is six-coordinate with distorted octahedral geometry (Robinson, Wilkins & Zhang, 1990), indium in (1) is four-coordinate in a distorted tetrahedron. The In—O bond length of 2.261 (3) Å is longer than those in InCl₃(Me₃PO)₃ [2.164 (11) Å], InCl₃(Me₃PO)₂(MeOH) [2.155 (4) Å] and [InCl₃(Me₃PO)₂(H₂O)]H₂O [2.157 (5) Å]. The trigonal Me₃In molecule undergoes only slight pyramidalization upon coordination of the phosphine oxide [C—In—C = 116.1 (2)–120.7 (2)°], and therefore no significant change in In—C distances [2.16 (4)–2.25 (6) Å for Me₃In (Vranka & Amma, 1967) and 2.158 (5)–2.168 (5) Å for (1)] was observed. These data suggest weak interaction between the indium centre and the O atom. Although there are no crystal data available for 5-benzylidibenzo[*b,d*]phosphole 5-oxide, the P—O bond distance for the oxide should be comparable with that of Ph₃PO. The P—O distance in (1) [1.481 (3) Å] is almost the same as the P—O bond distance for free Ph₃PO [1.484 (1) Å] (Spek, 1987), which should imply only weak π delocalization over P—O—In, if any. In stark contrast to the Al—O—P and Ga—O—P linear linkages in AlMe₃.OPPh₃ (Feher, Budzichowski & Weller, 1993), AlCl₃.OPPh₃ and GaCl₃.OPPh₃ (Burford *et al.*, 1990), In—O—P in (1) is bent with an In—O—P bond angle of 135.9 (2)°. This agrees well with the idea of weak π delocalization over the In—O—P linkage. The P centre in (1) has distorted tetrahedral geometry. Although the P-containing five-membered ring is nearly planar, normal P—C(2) and P—C(12) single-bond distances indicate non-aromatic character of the ring.

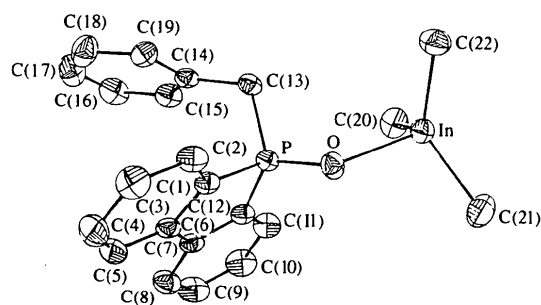


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

All manipulations were performed in a glove box under purified nitrogen. Solvents were heated under reflux with sodium benzophenone and distilled under nitrogen prior to use. 5-Benzyldibenz[*b,d*]phosphole 5-oxide was mixed with trimethylindium in benzene at room temperature. After stirring the mixture at 323 K for 2 h, most of the solvent was removed in vacuum and a white precipitate filtered off. Crystals were obtained by recrystallization from benzene and petroleum ether (303–333 K) (1:2) mixture.

Crystal data

[In(CH₃)₃(C₁₉H₁₅OP)]

$M_r = 450.22$

Triclinic

$P\bar{1}$

$a = 9.089$ (2) Å

$b = 9.418$ (3) Å

$c = 12.575$ (8) Å

$\alpha = 89.45$ (4)°

$\beta = 105.25$ (3)°

$\gamma = 91.85$ (2)°

$V = 1038.0$ (8) Å³

$Z = 2$

$D_x = 1.44$ Mg m⁻³

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (Molecular Structure Corporation, 1987)

$T_{\min} = 0.948$, $T_{\max} = 1.000$

3896 measured reflections

3641 independent reflections

Refinement

Refinement on F

$R = 0.044$

$\omega R = 0.057$

$S = 1.90$

3353 reflections

226 parameters

H-atom parameters not refined

$w = 1/\sigma^2(F)$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 10.26$ – 16.94 °

$\mu = 1.202$ mm⁻¹

$T = 296$ K

Prism

$0.90 \times 0.70 \times 0.40$ mm

Colourless

3353 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.0117$

$\theta_{\max} = 25$ °

$h = 0 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 14$

3 standard reflections

monitored every 300

reflections

intensity decay: 1.7%

$(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\max} = 0.76$ e Å⁻³

$\Delta\rho_{\min} = -1.03$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

C(4)	0.8918 (6)	0.7971 (5)	0.4698 (4)	5.5 (2)
C(5)	0.8158 (6)	0.6743 (5)	0.4911 (3)	4.7 (2)
C(6)	0.8082 (4)	0.5559 (4)	0.4256 (3)	3.3 (1)
C(7)	0.7367 (4)	0.4159 (4)	0.4355 (3)	3.6 (1)
C(8)	0.6629 (5)	0.3751 (5)	0.5158 (3)	5.1 (2)
C(9)	0.6065 (6)	0.2379 (6)	0.5157 (4)	6.1 (2)
C(10)	0.6204 (6)	0.1411 (5)	0.4380 (4)	5.9 (2)
C(11)	0.6915 (5)	0.1806 (5)	0.3571 (4)	4.8 (2)
C(12)	0.7468 (4)	0.3183 (4)	0.3569 (3)	3.4 (1)
C(13)	0.6972 (4)	0.4348 (4)	0.1331 (3)	3.7 (1)
C(14)	0.5699 (4)	0.5207 (4)	0.1488 (3)	3.4 (1)
C(15)	0.4430 (5)	0.4572 (5)	0.1731 (3)	4.5 (2)
C(16)	0.3291 (5)	0.5392 (7)	0.1914 (4)	5.9 (2)
C(17)	0.3390 (6)	0.6834 (7)	0.1854 (5)	6.4 (2)
C(18)	0.4625 (6)	0.7473 (5)	0.1607 (5)	6.0 (2)
C(19)	0.5766 (5)	0.6656 (4)	0.1410 (3)	4.4 (2)
C(20)	0.7997 (6)	0.0373 (5)	0.1023 (4)	5.8 (2)
C(21)	1.2176 (6)	0.0777 (6)	0.2467 (5)	6.3 (2)
C(22)	1.0507 (6)	0.2870 (6)	-0.0004 (4)	5.7 (2)

Table 2. Selected geometric parameters (Å, °)

In—C(22)	2.158 (5)	In—O	2.261 (3)
In—C(20)	2.168 (5)	P—C(1)	1.793 (4)
P—O	1.481 (3)	P—C(13)	1.819 (4)
P—C(12)	1.800 (3)	C(6)—C(7)	1.469 (5)
In—C(21)	2.161 (5)		
C(22)—In—C(21)	116.1 (2)	C(22)—In—C(20)	116.6 (2)
C(22)—In—O	98.4 (2)	C(21)—In—C(20)	120.7 (2)
C(21)—In—O	96.3 (2)	C(20)—In—O	100.9 (2)
O—P—C(1)	116.4 (2)	O—P—C(12)	117.4 (2)
O—P—C(13)	112.1 (2)	C(1)—P—C(12)	93.1 (2)
C(1)—P—C(13)	107.5 (2)	C(12)—P—C(13)	108.5 (2)
P—O—In	135.9 (2)	C(2)—C(1)—C(6)	121.5 (3)
C(2)—C(1)—P	129.2 (3)	C(6)—C(1)—P	109.2 (3)
C(5)—C(6)—C(1)	118.4 (4)	C(5)—C(6)—C(7)	128.2 (3)
C(1)—C(6)—C(7)	113.3 (3)	C(12)—C(7)—C(8)	118.8 (4)
C(12)—C(7)—C(6)	114.9 (3)	C(8)—C(7)—C(6)	126.3 (4)
C(11)—C(12)—C(7)	122.3 (3)	C(11)—C(12)—P	128.4 (3)
C(7)—C(12)—P	109.2 (3)		

The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques. H atoms were placed in calculated positions and not used for correction of the structure.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1987). Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1984). Program(s) used to refine structure: *TEXSAN LS*, *TEXSAN FOUR*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: KH1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

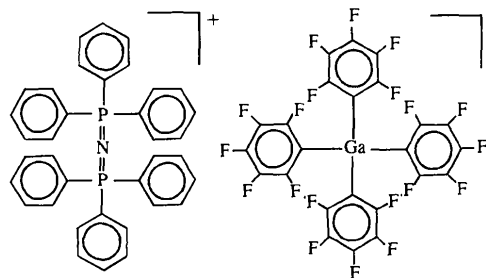
	x	y	z	B_{eq}
In	1.01482 (3)	0.15638 (3)	0.13305 (2)	3.99 (2)
P	0.8401 (1)	0.4013 (1)	0.26165 (7)	3.07 (3)
O	0.9748 (3)	0.3312 (3)	0.2433 (2)	4.2 (1)
C(1)	0.8767 (4)	0.5646 (4)	0.3375 (3)	3.3 (1)
C(2)	0.9508 (5)	0.6873 (4)	0.3163 (3)	4.3 (2)
C(3)	0.9565 (6)	0.8041 (5)	0.3826 (4)	5.3 (2)

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wenig größer als der Mittelwert [$142,2(3)^\circ$] von 497 Eintragungen in der CSD (Allen, Kennard & Taylor, 1983). Im Anion $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$ ist das zentrale Gallium-Atom ungefähr tetraedrisch von den Pentafluorphenylgruppen koordiniert [Mittelwert C—Ga—C = $110(2)^\circ$]. Die Gallium-Kohlenstoff-Abstände variieren geringfügig [$1,984(8)$ bis $2,039(8)$ Å] und bleiben größer als der Mittelwert über die Abstände Ga—C in Vergleichstrukturen mit Gallium-Kohlenstoff-Bindungen [Ga—C = $1,985(2)$ Å für 760 Fragmente in 290 Verbindungen aus der CSD].



(I)

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Bis(triphenylphosphin)iminium-Tetrakis(pentafluorphenyl)gallat

KARL-FRIEDRICH TEBBE, THEO GILLES, FRANK CONRAD UND WIELAND TYRRA

Institut für Anorganische Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Deutschland. E-mail: tebbe@rrz.uni-koeln.de

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Abstract

The crystal structure of bis(triphenylphosphine)iminium tetrakis(pentafluorophenyl)gallate, $[\text{N}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2][\text{Ga}(\text{C}_6\text{F}_5)_4]$, has been determined by X-ray diffraction methods. The tetrakis(pentafluorophenyl)gallate anion has almost tetrahedral geometry.

Kommentar

Die Kristallstruktur des Salzes $[\text{PNP}][\text{Ga}(\text{C}_6\text{F}_5)_4]$ enthält das Kation $[\text{PNP}]^+$ und das Anion $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$ jeweils auf allgemeinen Lagen (Fig. 1). Das Kation zeigt keine strukturellen Besonderheiten. Der zentrale Bindungswinkel, $\text{P1—N—P2} = 146,2(4)^\circ$, ist nur

Ein isoliertes Tetraorganylgallat-Anion $[\text{GaR}_4]^-$ ist bisher offensichtlich noch nicht strukturell charakterisiert worden, so daß Vergleichsdaten fehlen. In der analogen Gold-Verbindung Bis(triphenylphosphin)iminium-Tetrakis(pentafluorphenyl)gold(III) (Murray *et al.*, 1987) ist das Gold-Atom quadratisch planar koordiniert. Die Verbindung Tetrakis(μ_2 -dimethylendi-phenylphosphin)-tetrakis(pentafluorphenyl)pentagold-(I,II,III) Tetrakis(pentafluorphenyl)gold Dichlormethan-Solvat (Usón, Laguna, Laguna, Jiménez & Jones, 1991) enthält ebenfalls das quadratisch planare Anion $[\text{Au}(\text{C}_6\text{F}_5)_4]^-$. Die drei isostrukturellen Verbindungen Tetrakis(pentafluorphenyl)silan (Karipides & Forster, 1978), Tetrakis(pentafluorphenyl)germanium und Tetrakis(pentafluorphenyl)zinn (Karipides, Forman, Thomas & Reed, 1974) sind wie das Tetrakis(pentafluorphenyl)borat-Anion tetraedrisch aufgebaut. In den sechs bisher strukturell charakterisierten Verbindungen mit ausschließlicher Verknüpfung des Galliums mit vier C-Atomen Tetramethyl-bis(μ_2 -phenylethynyl)digallium (Teclé, Ilesley & Oliver, 1981), [Methanido-bis(dimethylphosphonium-methylid)]-dimethylgallium (Schmidbauer, Gasser, Krüger & Sekutowski, 1977), (μ_2 -1,4-Dioxan-*O,O'*)bis{bis(μ_2 -trimethylsilylmethylen)-(1,4-dioxan-*O*)-bis(trimethylsilyl)methyl]-gallium-lithium} (Uhl, Klinkhammer, Layh & Massa, 1991), Bis[1,1-(μ_2 -dimethylgallium)]diferrocen (Lee, Pennington, Laske & Robinson, 1990), Bis(η^5 -cyclopentadienyl)-(μ_2 -methyl)dimethyl(μ_2 - σ^3 -cyclohexen-1,1,2-triyl)gallium-zirconium (Erker, Albrecht, Krüger & Werner, 1992) und Bis(η^5 -cyclopentadienyl)-(μ_2 -methyl)-dimethyl-(μ_2 - σ^3 -benzol-1,1,2-triyl)-gallium-zirconium (Erker *et al.*, 1992) ist das Gallium ausnahmslos Teil eines Ringsystems.