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Structures of the Indium Trihalide Bisphosphine Complexes $[InBr_3(PMe_2Ph)_2]$ and $[InI_3(PMePh_2)_2]$

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Abstract

Both title compounds, tribromobis(dimethylphenylphosphine)indium and triiodobis(methyldiphenylphosphine)-indium, contain indium(III) in a trigonal bipyramidal environment, with axial phosphine and equatorial halide ligands. In—P bonds are *ca* 0.1 Å longer in the triiodide compound; this probably results mainly from the larger size of the phosphines in this compound, although the effect of changing the halide cannot be assessed from the limited data available. Deviations of angles from ideal trigonal bipyramidal values are statistically significant but no larger than those commonly observed for this type of geometry.

Comment

Phosphine complexes of the *p*-block elements have been known for many years and the subject has been reviewed (Levason & McAuliffe, 1976), but the number of compounds which have been structurally characterized remains small. For the specific example of indium(III) halides (X = halogen), the following types of complex have been proposed on the basis of analytical and spectroscopic data: $[InX_3(PR_3)_n]$ (n = 1, 2, 3), $[InX_2(PR_3)_n]^+$ (n = 2, 4) and $[In(PR_3)_4]^{3+}$ (Carty & Tuck, 1975). However, the only compounds to have been structurally characterized are the 1:1 adducts $[InI_3(PHPh_2)]$ (1) and $[InI_3(PH^tBu_2)]$ (2) (Alcock, Degnan, Howarth & Wallbridge, 1992), and the 2:1 adducts $[InCl_3(PPh_3)_2]$ (3) (Veidis & Palenik, 1969), $[InCl_3(PMe_3)_2]$ (4) and $[(InI_3)_2(Ph_2PCH_2CH_2PPh_2)_3]$ (5) (Degnan, Alcock, Roe & Wallbridge, 1992). In the former set of complexes, the indium adopts a tetrahedral geometry, while in the latter set the geometry is trigonal bipyramidal with *trans* axial phosphines. In (5), one diphosphine ligand bridges the two indium centres, whereas the other two are monodentate. Also worth mentioning is the related 1:1 gallium complex $[GaCl_3(PMe_3)]$ (Carter, Jugie, Enjalbert & Galy, 1978). We report here the structures of the two indium trihalide bisphosphine adducts $[InBr_3(PMe_2Ph)_2]$ (6) and $[InI_3(PMePh_2)_2]$ (7).

The indium centre in both molecules adopts a trigonal bipyramidal geometry with the phosphine ligands *trans* in the axial sites. The In—P bond distances in (6) are 2.614 (3) and 2.622 (3) Å, but are *ca* 0.1 Å longer in (7) at 2.712 (3) and 2.719 (3) Å. We note that in (5), the In—P bond distances are longer still at 2.798 (3) and 2.819 (2) Å, whereas those in (4) are 2.575 (3) and 2.576 (3) Å, the shortest bonds between InX_3 and PR_3 in any structure to date; in (3) the relevant bond lengths are 2.701 and 2.723 Å. Clearly, the wide range of observed values reflects the large variation in the size of the phosphines, but the nature of the halide is also likely to be important. Additional structures in which the phosphine is varied while the halide is kept constant, and structures of complexes of different indium(III) halides with the same phosphine, would allow the various factors to be delineated more clearly. The In—P bond lengths in the tetrahedral complexes (1) and (2) are 2.598 (mean of two independent molecules)

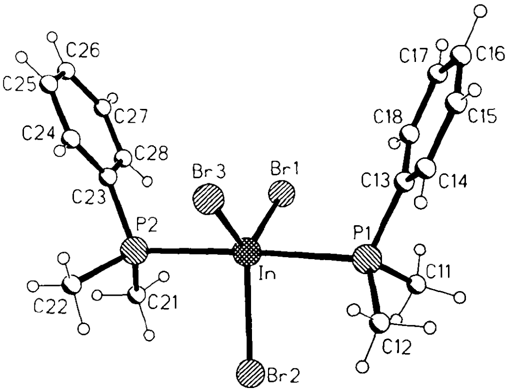

Fig. 1. Molecular structure of (6).

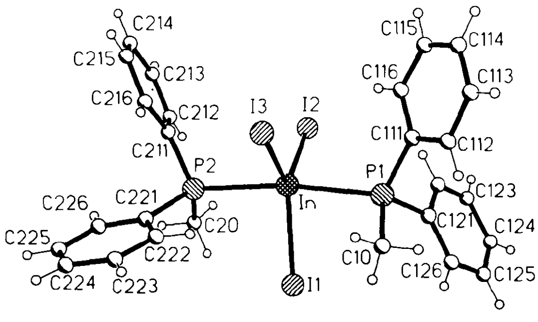

Fig. 2. Molecular structure of (7).

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and 2.586 Å, respectively, which are both somewhat shorter than the In—P bonds in the triiodide bisphosphine complexes (5) and (7); this undoubtedly reflects the difference in coordination number.

The P—In—P bond angles are 177.34 (8) and 169.82 (9)° for (6) and (7), respectively, which are not markedly different from the values found for (3)-(5), ranging from 173.0 to 175.6°. The angles between the axial and equatorial ligands in (6) and (7) are all within a few degrees of the ideal value of 90°, but the inter-equatorial X—In—X angles range from 113.98 (6) to 125.16 (5)° for (6) and from 114.32 (4) to 128.87 (4)° for (7); deviations from 120° of this magnitude are not uncommon in trigonal bipyramidal complexes.

Experimental

Compound (6)

Crystal data

$[\mathrm{InBr_3(C_8H_{11}P)_2}]$
M_r = 630.83
Monoclinic
$P2_1/c$
a = 17.071 (6) Å
b = 9.368 (4) Å
c = 14.566 (9) Å
β = 107.95 (5)°
V = 2216.0 (18) Å^3
Z = 4
D_x = 1.891 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 27 reflections
θ = 10.08 - 12.80°
μ = 6.615 mm^{-1}
T = 160.0 (10) K
Block
0.40 × 0.30 × 0.28 mm
Colourless

Data collection

Stoe Siemens diffractometer
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: empirical
$T_{\min}$ = 0.112, $T_{\max}$ = 0.156
3882 measured reflections
3882 independent reflections

2747 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max}$ = 25.00°
h = 0 → 20
k = −11 → 0
l = −17 → 16
5 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0575
$wR(F^2)$ = 0.1700 (all data)
S = 1.130 (all data)
3879 reflections
204 parameters
H atoms constrained
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.1061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max}$ = 1.84 e Å^{-3}
$\Delta\rho_{\min}$ = −1.58 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0027 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (6)

$$U_{\mathrm{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
In	0.24336 (4)	0.70137 (6)	0.30443 (4)	0.0261 (4)
Br1	0.25490 (6)	0.77981 (10)	0.14041 (7)	0.0371 (6)
Br2	0.14585 (6)	0.86061 (11)	0.36772 (6)	0.0366 (5)
Br3	0.31489 (6)	0.48151 (11)	0.40062 (7)	0.0397 (6)
P1	0.11482 (14)	0.5433 (3)	0.2188 (2)	0.0293 (12)
P2	0.36687 (15)	0.8675 (3)	0.3917 (2)	0.0332 (12)
C11	0.0392 (6)	0.6388 (11)	0.1250 (7)	0.041 (5)
C12	0.0621 (6)	0.4878 (12)	0.3045 (7)	0.042 (5)
C13	0.1364 (5)	0.3830 (9)	0.1602 (6)	0.030 (5)
C14	0.1288 (7)	0.2462 (11)	0.1959 (8)	0.043 (6)
C15	0.1465 (7)	0.1287 (10)	0.1484 (8)	0.046 (7)
C16	0.1731 (6)	0.1439 (11)	0.0693 (7)	0.042 (6)
C17	0.1812 (6)	0.2789 (10)	0.0342 (7)	0.037 (6)
C18	0.1644 (6)	0.3977 (9)	0.0817 (6)	0.031 (5)
C21	0.3359 (7)	1.0517 (11)	0.3659 (9)	0.050 (7)
C22	0.3995 (7)	0.8522 (15)	0.5214 (8)	0.054 (6)
C23	0.4583 (6)	0.8450 (10)	0.3546 (6)	0.030 (5)
C24	0.5200 (6)	0.7517 (11)	0.4041 (7)	0.036 (5)
C25	0.5922 (6)	0.7393 (12)	0.3782 (8)	0.043 (5)
C26	0.6003 (6)	0.8187 (11)	0.3015 (7)	0.038 (5)
C27	0.5378 (6)	0.9078 (11)	0.2505 (7)	0.042 (6)
C28	0.4671 (6)	0.9203 (12)	0.2767 (7)	0.040 (5)

Table 2. *Selected geometric parameters* (Å, °) *for* (6)

In—P2	2.614 (3)	P1—C13	1.820 (9)
In—P1	2.622 (3)	P1—C12	1.825 (9)
In—Br1	2.565 (2)	P2—C22	1.803 (11)
In—Br3	2.577 (2)	P2—C21	1.810 (11)
In—Br2	2.606 (2)	P2—C23	1.815 (9)
P1—C11	1.802 (10)		
P2—In—P1	177.34 (8)	C11—P1—C12	105.7 (5)
Br1—In—Br3	125.16 (5)	C13—P1—C12	107.4 (5)
Br1—In—Br2	113.98 (6)	C11—P1—In	112.3 (3)
Br3—In—Br2	120.83 (6)	C13—P1—In	115.4 (3)
Br1—In—P2	90.03 (7)	C12—P1—In	110.6 (3)
Br3—In—P2	92.02 (8)	C22—P2—C21	105.6 (6)
Br2—In—P2	89.69 (8)	C22—P2—C23	106.7 (5)
Br1—In—P1	90.68 (7)	C21—P2—C23	105.7 (5)
Br3—In—P1	89.66 (8)	C22—P2—In	113.9 (4)
Br2—In—P1	87.68 (7)	C21—P2—In	109.1 (4)
C11—P1—C13	104.8 (4)	C23—P2—In	115.1 (3)

Compound (7)

Crystal data

$[\mathrm{InI_3(C_{13}H_{13}P)_2}]$
M_r = 895.93
Orthorhombic
$Pna2_1$
a = 14.758 (3) Å
b = 22.038 (4) Å
c = 8.977 (2) Å
V = 2919.7 (10) Å^3
Z = 4
D_x = 2.038 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 12.15 - 12.50°
μ = 4.104 mm^{-1}
T = 160.0 (10) K
Block
0.48 × 0.48 × 0.26 mm
Colourless

Data collection

Stoe Siemens diffractometer
ω/θ scans

R_{int} = 0.0322 (on F^2)
$\theta_{\max}$ = 25.03°

Absorption correction:
empirical
T_{min} = 0.096, T_{max} = 0.167
4456 measured reflections
4099 independent reflections
3724 observed reflections
$[I > 2\sigma(I)]$

$h = -17 \rightarrow 17$
$k = 0 \rightarrow 26$
$l = -5 \rightarrow 10$
5 standard reflections
frequency: 60 min
intensity variation: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0316$
$wR(F^2) = 0.1120$ (all data)
$S = 1.119$ (all data)
4089 reflections
290 parameters
H atoms constrained
Calculated weights
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 43.2185P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Extinction correction:
*SHELXL*92 (Sheldrick, 1992)
Extinction coefficient:
0.00032 (9)
Atomic scattering factors
from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration:
Flack (1983); x = 0.16 (9)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (7)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
In	0.73574 (5)	0.65003 (4)	0.40563 (10)	0.0171 (3)
I1	0.86848 (6)	0.69253 (4)	0.21295 (13)	0.0317 (4)
I2	0.55976 (5)	0.66152 (4)	0.31389 (12)	0.0266 (3)
I3	0.75577 (5)	0.59769 (4)	0.68320 (11)	0.0262 (4)
P1	0.7557 (2)	0.75761 (14)	0.5502 (4)	0.0188 (14)
P2	0.7481 (2)	0.54100 (15)	0.2670 (4)	0.0184 (14)
C10	0.8754 (8)	0.7646 (6)	0.5987 (17)	0.026 (6)
C111	0.6954 (8)	0.7669 (5)	0.7294 (14)	0.018 (6)
C112	0.7342 (9)	0.7981 (7)	0.8472 (18)	0.035 (6)
C113	0.6869 (10)	0.8017 (7)	0.9830 (18)	0.036 (7)
C114	0.6019 (10)	0.7791 (7)	0.9933 (18)	0.034 (8)
C115	0.5624 (9)	0.7502 (6)	0.8761 (16)	0.030 (7)
C116	0.6090 (8)	0.7422 (6)	0.7432 (17)	0.028 (7)
C121	0.7287 (8)	0.8260 (6)	0.4454 (16)	0.025 (6)
C122	0.6378 (8)	0.8358 (5)	0.3980 (16)	0.024 (6)
C123	0.6142 (9)	0.8846 (6)	0.3133 (19)	0.033 (7)
C124	0.6801 (10)	0.9267 (7)	0.2766 (20)	0.041 (8)
C125	0.7701 (10)	0.9183 (6)	0.3190 (20)	0.038 (8)
C126	0.7940 (8)	0.8677 (5)	0.3987 (17)	0.025 (6)
C20	0.7468 (9)	0.5543 (6)	0.0666 (16)	0.026 (7)
C211	0.6544 (7)	0.4902 (5)	0.3023 (16)	0.019 (5)
C212	0.5810 (9)	0.4853 (6)	0.2037 (23)	0.040 (7)
C213	0.5083 (9)	0.4468 (8)	0.2378 (24)	0.052 (7)
C214	0.5095 (10)	0.4112 (6)	0.3692 (23)	0.045 (7)
C215	0.5818 (10)	0.4153 (6)	0.4603 (20)	0.038 (9)
C216	0.6560 (8)	0.4536 (6)	0.4277 (19)	0.033 (6)
C221	0.8501 (7)	0.4953 (5)	0.3014 (16)	0.020 (5)
C222	0.9129 (9)	0.5136 (7)	0.4037 (20)	0.036 (6)
C223	0.9872 (8)	0.4771 (7)	0.4321 (20)	0.038 (6)
C224	1.0008 (8)	0.4245 (6)	0.3584 (20)	0.036 (5)
C225	0.9389 (8)	0.4069 (6)	0.2430 (18)	0.031 (6)
C226	0.8626 (8)	0.4426 (5)	0.2166 (19)	0.026 (6)

Table 4. *Selected geometric parameters* (Å, °) *for* (7)

In—P2	2.712 (3)	P1—C10	1.826 (12)
In—P1	2.719 (3)	P1—C111	1.851 (13)
In—I2	2.7362 (14)	P2—C211	1.807 (12)
In—I3	2.762 (2)	P2—C20	1.822 (15)
In—I1	2.776 (2)	P2—C221	1.836 (11)
P1—C121	1.822 (14)		
P2—In—P1	169.82 (9)	C121—P1—C111	104.6 (6)
P2—In—I2	90.45 (7)	C10—P1—C111	104.4 (6)
P1—In—I2	99.55 (7)	C121—P1—In	116.9 (5)
P2—In—I3	92.11 (8)	C10—P1—In	107.0 (5)
P1—In—I3	85.52 (8)	C111—P1—In	117.3 (4)
I2—In—I3	114.32 (4)	C211—P2—C20	105.3 (6)
P2—In—I1	88.01 (8)	C211—P2—C221	104.9 (5)
P1—In—I1	85.79 (8)	C20—P2—C221	105.3 (6)
I2—In—I1	116.81 (5)	C211—P2—In	114.6 (4)
I3—In—I1	128.87 (4)	C20—P2—In	108.0 (4)
C121—P1—C10	105.4 (6)	C221—P2—In	117.6 (4)

Compounds (6) and (7) were prepared according to literature methods (Carty, Hinsperger & Boorman, 1970; Roundhill, 1971). Diffraction-quality crystals were obtained by solvent diffusion of hexane into tetrahydrofuran solutions at 243 K.

For both structures, the H atoms were constrained: phenyl C—H = 0.94 Å on ring-angle bisectors with $U(H) = 1.2U_{eq}(C)$; methyl C—H = 0.99 Å, H—C—H = 109.5°, staggered conformations with $U(H) = 1.5U_{eq}(C)$. The absolute structure determination is based on the enantiomorph polarity parameter method of Flack (1983); the data set includes Friedel pairs for all reflections with $|l| \leq 5$. Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL*/*PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC*. Software used to prepare material for publication: *SHELXL*93 and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71460 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1062]

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