Indium Triiodide Complexes of Bis(diphenylphosphino)ethane (dppe) and its Disulfide (dppeS₂)

Marcus Sigl, Annette Schier, Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Z. Naturforsch. 54 b, 21-25 (1999); received October 10, 1998

Indium Triiodide, Phosphine Complexes, Phosphine Sulfide Complexes, Conformation, Crystal Structure

Bis(diphenylphosphino)ethane (dppe) and its disulfide $(dppeS_2)$ react with two equivalents of indium triiodide to give high yields of the corresponding 1:2 adducts. According to crystal structure determinations, both compounds are molecular bis-terminal complexes with the ligands in an all-trans conformation. Contrary to previous findings for complexes of the indium trihalides and of GaBr₃ and GaI₃ with ditertiary phosphines in fixed cis-structure [bis(diphenylphosphino)ethene or -benzene], no iodide redistribution is observed to give the ionic species [(dppe)InI₂]⁺ [InI₄]⁻. The molecular structures are also retained in solution.

Introduction

The trihalides of the Group III elements EX_3 are strong Lewis acids with a high potential as catalysts [1]. The catalytic activity can be modified by carefully selecting the right central metal (E = B, Al, Ga, In, Tl) and halogen (X = F, Cl, Br, I), but also by auxiliary ligands L which may reduce the acceptor properties to make reactions more selective under mild conditions [2]. The role of the ligand L is often played by the solvent molecules, typically diethylether or tetrahydrofuran, or by an auxiliary component like a dialkylsulfide or a tertiary phosphine.

While such complexes X_3E-L are well documented for the boron and aluminium halides (E = B, Al), the corresponding gallium and indium compounds (E = Ga, In) have received much less attention [3]. Since there is current interest in the usage of gallium and indium halides as more selective reaction promotors [4], a systematic study of the stoichiometry, properties and structure of complexes of these halides with phosphines is currently under way [5].

Tertiary phosphines are versatile ligands which are commercially available in a large variety of functionalities. Ditertiary compounds are particularly attractive, because they may act as bridging and chelating ligands depending mainly on the relative sizes of the ligand span and the radius of the metal. Our initial studies with the gallium and indium trihalides have shown a rich structural diversity, including both molecular and ionic complexes with various ring sizes and coordination numbers (CN) [6]. While in phosphine complexes of InCl₃ and InBr₃ the metal atom reaches CN 6, the maximum CN for the adducts with InI₃ is limited to 5, probably owing to steric congestion.

In order to probe further the ligand capabilities of diphosphines towards InI₃ we employed bis(diphenylphosphino)ethane (dppe) and its disulfide (dppe S_2) as ligands, where a flexible hydrocarbon loop between the donor centers should allow for a better match of the components. InI₃ is known to form a molecular 1:2 complex with PPh₃, the indium atom of which is in a trigonal bipyramidal coordination environment with the two phosphines occupying the apical positions [5b]. The literature contains also a report of the 1:1 complex of InI₃ and dppe which appears as a coordination polymer $[(dppe)InI_3]_x$, again with pentacoordinate indium atoms. The 2:3 complex represents a segment of this polymer (dppe)InI₃(dppe)InI₃(dppe) with two free terminal phosphino functions [5c]. The 2:1 complex has also been prepared previously, but its structure is yet unknown [5b, d, e, f].

^{*} Reprint requests to Prof. Dr. H. Schmidbaur.

^{0932–0776/99/0100–0021 \$ 06.00 © 1999} Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com



Results

Two equivalents of indium triiodide react with one equivalent of (dppe) or (dppeS₂) in anhydrous toluene at 80°C to give high yields of the expected 1:2 complexes as colourless crystals with high melting points (1: m.p. 241°C, 2: m.p. 226 °C, with decomposition).

Both compounds are very sensitive to moisture as solids and in solution and must be handled in a rigorously dried inert atmosphere.

Solutions of compound **1** in dichloromethane show in the ${}^{31}P{}^{1}H{}$ NMR spectrum a singlet reso-



Fig. 1. Molecular structure of compound **1**.(ORTEP drawing with 50% probability ellipsoids, H-atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: In1-P1 2.6035(12), In1-I1 2.6523(6). In1-I2 2.6833(5), In1-I3 2.7023(6), In2-P2 2.5966(12), In2-I4 2.6843(6), In2-I5 2.6773(5), In2-I6 2.6685(5), P1-C1 1.836(4), C1-C2 1.530(6), C2-P2 1.828(4); P1-In1-I1 108.95(3), P1-In1-I2 98.59(3), P1-In1-I3 103.41(3), I1-In1-I2 120.73(2), I1-In1-I3 112.20(2), I2-In1-I3 110.65(2), P2-In2-I4 104.84(3), P2-In2-I5 117.15(2), P2-In2-I6 106.53(3), I4-In2-I5 113.78(2), I4-In2-I6 113.31(2), I5-In2-I6 117.15(2).

nance which appears at much higher field (δ -27.1) than the resonance of the parent ligand (δ -12.5). This is an unusual phenomenon for phosphine coordination to most Main Group and Transition Metals, but there is precedent for the same effect in the particular case of other heavy Main Group Metals, including gallium and indium trihalide complexes [6]. It therefore appears that this behaviour is common for Main Group Metals in the lower parts of the Periodic Table. Several high level theoretical studies are currently under way in several laboratories to rationalize the data in terms of the electronic characteristics of heavy elements.

Solutions of compound **2** in chloroform also show only a singlet signal in the ${}^{31}P{}^{1}H{}$ NMR spectrum (δ 48.9), but only slightly shifted down-field relative to the resonance of free (dppeS₂) because the coordination does not occur at the phosphorus center. The ${}^{1}H{}$ and ${}^{13}C{}^{1}H{}$ NMR spectra of **1** and **2** show no anomalies and are not significantly temperaturedependent.

Crystals of **1** are monoclinic, space group $P2_1/n$, with Z = 4 formula units in the unit cell. The lattice is composed of individual molecules with no sub-van der Waals contacts. The molecules have no crystallographically imposed symmetry, but the structure approaches quite closely the symmetry



Fig. 2. Molecular structure of compound **2**.(ORTEP drawing with 50% probability ellipsoids, Ph-*H* atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: In-S1 2.5322(13), In-I1 2.6859(5), In-I2 2.6901(6), In-I3 2.6733(5), P1-S1 2.011(2), P1-C1 1.807(5), C1-C1' 1.521(9); S1-In-I1 98.88(3), S1-In-I2 109.58(4), S1-In-I3 108.06(4), I1-In-I2 110.00(2), I1-In-I3 111.47(2), I2-In-I3 117.24(2), In-S1-P1 111.11(6).

	1	2
Crystal data		
Formula	$C_{26}H_{24}I_6In_2P_2$	$C_{26}H_{24}I_6In_2P_2S_2$
Mr	1389.43	1453.55
Crystal system	monoclinic	monoclinic
Space group	$P2_{1}/n$	$P2_{1}/c$
$a\left(\overset{\mathbf{A}}{\overset{\circ}{\mathbf{A}}} \right)$	10.460(1)	12.184(1)
$b(\mathbf{A})$	15.481(1)	14.640(1)
$c(\mathbf{A})$	22.920(2)	11.962(1)
α (°)	90	90
β (°)	98.67(1)	114.97(1)
γ (°).	90	90
$V(Å^3)$	3669.1(5)	1934.3(3)
$\rho_{\rm calc} ({\rm gcm}^{-3})$	2.515	2.496
Z	4	2
F(000)	2515	1316
$\mu(\mathrm{Mo}K_{\alpha})(\mathrm{cm}^{-1})$	64.08	61.87
Data collection		
$T(^{\circ}C)$	-74	+21
Scan mode	ω - Θ	ω - 2 Θ
hkl Range	$-12 \rightarrow 12, -10 \rightarrow 0, -28 \rightarrow 28$	$-14 \rightarrow 15, 0 \rightarrow 18, -15 \rightarrow 0$
$\sin(\theta/\lambda)_{\rm max}$ (Å ⁻¹)	0.62	0.62
Measured reflections	8479	3984
Unique reflections	$6624 [R_{int} = 0.0309]$	$3810 [R_{int} = 0.0200]$
Refls, used for refinement	6615	3801
Absorption correction	psi-scans	psi-scans
T_{min} / T_{max}	0 56/0 99	0.84/0.99
Refinement	0.0010.99	0.0 1/0.57
Refined parameters	325	180
Final <i>R</i> values $[I > 2\sigma(I)]$	525	180
$P1^{[a]}$	0.0275	0.0275
$\mu P 2^{[b]}$	0.0213	0.0275
which (shift/arror)		< 0.001
$(\sin \theta \cos \theta) \sin \theta \cos \theta$	1 125/ 1 442	0.725/ 0.742
$p_{\text{fin}}(\text{max/mm})$ (eA)	1.133/-1.442	0.7557-0.742

Table I. Crystal data, data collection, and structure refinement for compounds 1 and 2.

^[a] $R1 = \Sigma(||F_o| - |F_c|| / \Sigma|F_o|; |b| wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}; w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]; p = (F_o^2 + 2F_c^2)/3; a = 0.0269$ (1), 0.0245 (2); b = 9.84 (1), 3.09 (2).

requirements of an inversion center (point group C_i , Fig. 1). The ligand is in an extended staggered all-trans conformation. Both the phosphorus and indium atoms are strictly tetra-coordinated and show no significant distortions from tetrahedral geometries. It is most important to note that a structure of this type is found although there is a choice between this molecular form and an ionic alternative [(dppe)InI₂]⁺ [InI₄]⁻. The solubility properties and the NMR data are consistent with a non-ionic dinuclear structure also for the solution state.

Crystals of **2** are also monoclinic, space group $P2_1/c$, with Z = 2 formula units in the unit cell. The lattice contains individual molecules the structure of

which has a crystallographically imposed center of inversion (Fig. 2). This again calls for an extended ligand with tetrahedral chain members -PPh₂-CH₂-CH₂-PPh₂- in the staggered all-trans conformation. The InI₃ units are attached to the sulfur atoms with an angle P-S-In = $111.11(6)^{\circ}$. The dimensions of the InI₃ units are virtually the same in compounds **1** and **2**.

Conclusions

The present results have shown that both dppe and its disulfide form molecular dinuclear complexes with indium triiodide with quasi-centrosymmetrical structures involving extended all-trans ligands. According to low temperature ³¹P NMR studies there is no evidence for an equilibrium with ionic components in which the ligands are chelating a metal atom. This is at variance with the findings for the corresponding complexes of bidentate ligands in which the two donor centers are fixed in a cis position at a rigid backbone. It therefore appears that even within a closely analogous series of compounds there may be fundamental changes in the structural principle.

Experimental Part

All experiments were carried out in standard equipment with rigorous exclusion of air and moisture. The starting materials are commercially available. The dppeS₂ was prepared following a literature procedure [7].

$[1,2-Bis(diphenylphosphino)ethane](InI_3)_2$ (1)

Indium triiodide (307 mg, 0.619 mmol) is added to a solution of dppe (123 mg, 0.310 mmol) in 20 ml of toluene. The resulting mixture is stirred at 80°C for 1 h. Upon cooling to -30°C a colourless precipitate is formed which is collected after 1 d (0.31 g, 72% yield) and recrystallized from chloroform/pentane (m.p. 241°C). ¹H NMR (CD₂Cl₂, 20°C): δ 3.08 [d, J(P,H) = 3 Hz, 2 H, CH₂]; 7.53 - 7.94 (m, 10 H, Ph). ¹³C{¹H} NMR (v.s.): δ 23.9 [d, J(P,C) = 24 Hz, CH₂]; 121.9 [d, J(P,C) = 44 Hz, C_{ipso}], 130.6 [d, J = 11 Hz, C_{meta}], 133.7 [d, J = 10 Hz, C_{ortho}], 133.8 [s, C_{para}]. ³¹P{¹H} NMR (v.s.): δ -27.1 (br. s). ³¹P{¹H} NMR (CD₂Cl₂, -80°C): δ -25.7 (br. s).

 $C_{26}H_{24}I_6In_2P_2$ (1389.43)

Calcd C 22.47 H 1.74 %, Found C 21.94 H 1.62 %.

[1,2-Bis(diphenylphosphino)ethane disulfide](InI₃)₂ (2)

InI₃ (250 mg, 0.505 mmol) is added to a solution of dppeS₂ (117 mg, 0.252 mmol) in 10 ml of chloroform. The mixture is stirred for 10 h at 20°C. A colourless precipitate is formed (0.30 g, 82% yield), which is recrystallized from dichloromethane/diethylether (m.p. 226°C, decomp.).

¹H NMR (CDCl₃, 20°C): δ 2.45 (A₂XX'A'₂, 2 H, CH₂); 7.58 - 7.85 (m, 10 H, Ph). ¹³C{¹H} NMR (v.s.): δ 23.2 (AXX', CH₂); 123.8, 130.5, 132.4, 135.0 (all AXX', for Ph-C). ³¹P{¹H} NMR (v.s.): δ 48.9 (s).

 $C_{26}H_{24}I_6In_2P_2S_2$ (1453.55)

Calcd C 21.48 H 1.66 S 4.41 %, Found C 21.40 H 1.72 S 4.28 %.

Crystal structure determinations

Specimens of suitable quality and size of compounds 1 and 2 were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo- K_{α} radiation, λ (Mo- K_{α}) = 0.71073 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Lp correction was applied and intensity data were corrected for absorption effects. The structures were solved by direct methods and completed by full-matrixleast squares techniques against F². The thermal motion of all non-hydrogen atoms was treated anisotropically. All H atoms of compound 1 were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5$ x U_{eq} of the attached C atom), whereas the CH_2 atoms of compound 2 were located and refined with isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table I. Important interatomic distances and angles are shown in the corresponding Figure Captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 410282 (1) and 410283 (2).

Acknowledgement

This work was supported by Fonds der Chemischen Industrie. The authors are grateful to Mr. J. Riede for establishing the X-ray data sets.

25

- a) L. A. Paquette, Encyclopedia of Reagents for Organic Synthesis, p. 153, Wiley, New York (1995);
 b) J. A. Miller, in A. J. Downs, Chemistry of Aluminium, Gallium, Indium, and Thallium, p. 372, Chapman & Hall, London (1993).
- [2] a) J. A. Jegier, D. A. Atwood, Inorg. Chem. 36, 2034 (1997);

b) J. A. Jegier, D. A. Atwood, Inorg. Chem. **35**, 4277 (1996);

c) T. Aida, S. Inoue, Acc. Chem. Res. 29, 39 (1996);
d) Y. Hayashi, J. J. Rohde, E. J. Corey, J. Am. Chem. Soc. 118, 5502 (1996).

- [3] a) D. G. Tuck in A. J. Downs, Chemistry of Aluminium, Gallium, Indium, and Thallium, p. 430, Chapman & Hall, London (1993);
 b) D. G. Tuck in G. Wilkinson, R. D. Gillard, J. A. McCleverty, Comprehensive Coordination Chemistry, Vol. 3, 126, Pergamon Press, Oxford (1987);
 c) D. G. Tuck in G. Wilkinson, F. G. A. Stone, E. W. Abel, Comprehensive Organometallic Chemistry, Vol. 1, 683, Pergamon Press, Oxford (1982);
 d) A. J. Carty, D. G. Tuck in S. J. Lippard, Progress in Inorganic Chemistry, Vol. 19, 243, Wiley & Sons, New York (1975).
- [4] a) T.-P. Loh, J. Pei, G.-Q. Cao, J. Chem. Soc., Chem. Commun. 1996, 1819;

b) T.-P. Loh, J. Pei, M. Lin, J. Chem. Soc., Chem. Commun. **1996**, 2315;

c) H. Schmidbaur, W. Findeiß, Chem. Ber. **99**, 2187 (1966);

d) M. G. Voronkov, S. U. Basenko, Zh. Obshch. Khim. **65**, 1482 (1995).

- [5] a) M. A. Brown, J. A. Castro, D. G. Tuck, Can. J. Chem. 75, 333 (1997);
 - b) M. A. Brown, E. J. Wells, D. G. Tuck, Can. J. Chem. **74**, 1535 (1996);
 - c) I. A. Degnan, N. W. Alcock, S. M. Roe, M. G. H. Wallbridge, Acta Crystallogr. **C48**, 995 (1992);
 - d) A. J. Carty, Can. J. Chem. **45**, 345 (1967);
 - e) A. J. Carty, Can. J. Chem. 45, 3187 (1967);
 - f) A. Balls, N. N. Greenwood, B. P. Straughan, J. Chem. Soc. (A) **1968**, 753;
 - g) U. Flörke, H.-J. Haupt, Z. Kristallogr. 196, 299 (1991);
 - h) R. L. Wells, S. R. Aubuchon, S. S. Kher, M. S.
 - Lube, P. S. White, Chem. Mater. 7, 793 (1995);
 - i) M. V. Veidis, G. J. Palenik, J. Chem. Soc., Chem. Commun. **1969**, 586;
 - j) W. Clegg, N. C. Norman, N. L. Pickett, Acta Crystallogr. C50, 36 (1994);
 - k) N. W. Alcock, I. A. Degnan, O. W. Howarth, M. G. H. Wallbridge, J. Chem. Soc., Dalton Trans. 1992, 2775;
 - A. J. Carty, D. G. Duck, J. Chem. Soc. (A) 1966, 1081;
 - m) W. T. Robinson, C. J. Wilkins, Z. Zeying, J. Chem. Soc., Dalton Trans. **1988**, 2187.
- [6] a) M. Sigl, A. Schier, H. Schmidbaur, Eur. J. Inorg. Chem. 1998, 203;
 b) M. Sigl, A. Schier, H. Schmidbaur, Z. Naturforsch. 53b, (1998) submitted;

c) M. Sigl, A. Schier, H. Schmidbaur, Z. Naturforsch. **53b**, (1998) submitted.

[7] M. Preisenberger, A. Bauer, H. Schmidbaur, Chem. Ber. 130, 955 (1997).