# Lewis Acid Catalyzed Z to E Isomerization of 1,2-Bis(diphenylphosphino)ethene

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Z-1,2-Bis(diphenylphosphino)ethene, cis-Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>, forms 1:2 adducts with GaBr<sub>3</sub> and GaI<sub>3</sub>, the former of which has been identified in an X-ray diffraction study as the complex of the isomerized ligand, E-Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>. The GaI<sub>3</sub> complex is believed to be analogous on the basis of analytical and spectroscopic data. InBr<sub>3</sub> affords a 1:1 complex with an ionic structure  $[(Ph_2PCH=CHPPh_2)_2InBr_2]^+$   $[InBr_4]^-$  in which the cation contains the original *cis*-ligand. With InI<sub>3</sub> also a 1:1 adduct is obtained, where the metal triiodide unit is attached to only one phosphorus atom of the non-isomerized (cis) ligand in the solid state. There is rapid site exchange of the InI<sub>3</sub> unit in chloroform solution as followed by NMR spectroscopy. - The metal halide induced Z/E isomerization of Ph<sub>2</sub>PCH=CHPPh<sub>2</sub> has been studied in various solvents and at variable temperature with stoichiometric and catalytic amounts of AIX<sub>3</sub> and GaX<sub>3</sub> Lewis-acids. InX<sub>3</sub> compounds proved ineffective (X = Cl, Br, I). Anhydrous AIBr<sub>3</sub> was found to be most efficient, giving a 90% Z/E conversion in 10 min at 100°C in toluene. A mechanism is proposed which is compatible with the experimental data.

## Introduction

The aluminium trihalides are important catalysts for the rearrangement of hydrocarbons, cycloaddition reactions, Friedel-Crafts acylations, halogenations, and many other reactions [1]. Their action is based on the ability to coordinate as Lewis-acids to  $\pi$ -systems and heteroatoms [2]. Applications of the corresponding gallium trihalides are limited to only a few examples like the GaBr<sub>3</sub>-mediated methyl transfer between alkylsilanes and -siloxanes [3]. In the course of our studies of the reactivity of Group III metal halides controled by various Lewis-bases [4] we have now observed an olefin  $Z \rightarrow E$  isomerization induced by aluminium and gallium halides.

## **Preparative Results**

The reaction of two equivalents of anhydrous  $GaX_3$  (X = Br, I) with Z-1,2-bis(diphenylphosphino)ethene, Z-dppee, results in the formation of the dinuclear complexes of the Z  $\rightarrow$  E isomerized ligand (E-dppee)(GaX<sub>3</sub>)<sub>2</sub> (1) (eq. (1)). **1a** and **1b** are air-stable, but moisture-sensitive





crystalline products which are soluble in di- and trichloromethane. The structure has been confirmed by a crystal structure analysis of **1a**. The same conclusion has been drawn from NMR spectroscopy: After hydrolysis of the complexes the <sup>31</sup>P NMR spectra show only one resonance at -6 ppm which is in good agreement with literature data for E-dppee [5].

The ease of this isomerization is very astonishing since C=C double bonds in general are expected to be very robust. Although Z-dppee has been used as a chelating ligand in a large number of complexes and derivatives, only two isomerization reactions have been observed. Heating of Z-dppee dioxide or disulfide with PCl<sub>3</sub> results in the corresponding Edppee derivatives [6], and the binuclear gold complexes (Z-dppee)(AuX)<sub>2</sub> were found to isomerize upon photolysis to (E-dppee)(AuX)<sub>2</sub> (X = Cl, Br, I, *p*-SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) [7].

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The reaction of equimolar quantities of GaBr<sub>3</sub> /  $GaI_3$  and Z-dppee also results in the formation of 1 together with an equivalent of the non-coordinated dppee in E-configuration. This result demonstrates that the isomerization must be a catalytic process (eq. (2)). Further investigations have shown that GaCl<sub>3</sub> and AlBr<sub>3</sub> can also be applied, and that as little as 2 mol% are sufficient for more than 90% conversion in only 10 min (in toluene). Temperatures higher than 80°C are required (Table I). As a general rule catalytic activity increases with the standard Lewis-acidity of the metal trihalide. The best result was obtained with AlBr<sub>3</sub>, while indium trihalides do not show any catalytic activity at all. Control experiments in the dark established that the  $Z \rightarrow E$ -isomerization is no photochemical process.



Anhydrous  $InI_3$  reacts with equimolar quantities of Z-dppee to give almost quantitative yields of a colorless crystalline product (**2**, 94%, m.p. 249°C) which decomposes in water releasing free cis-phosphane ligand (eq. (3)). Single crystal structure analysis has shown that the complex is an unsymmetrical molecule with the indium atom connected to only one of the two phosphorus atoms. The structure is thus different from that of the analogous 1,2-bis(diphenylphosphino)benzene complex [4]. At variance with the solid state structure, the <sup>31</sup>P NMR spectrum shows only one resonance even at -90°C. This indicates a fast exchange of the InI<sub>3</sub> units between the two phosphorus atoms.



Unlike the results obtained with  $InI_3$ , the 1:1 addition compound of Z-dppee with  $InBr_3$  has an ionic structure (**3**, yield 92%, m.p. 202°C). The reaction

Table I. Isomerization of  $Z-1,2-Ph_2PCH=CHPPh_2$  in toluene.

Catalyst	Temperature	Time	Yield (NMR)
25 mol% GaBr3	80°C	3 h	68 %
25 mol% GaBr3	90°C	3 h	76 %
25 mol% GaBr3	90°C	6 h	94 %
5 mol% GaBr3	100°C	5 h	< 5 %
5 mol% GaCl3	100°C	5 h	13 %
2 mol% AlBr <sub>3</sub>	100°C	10 min	90 %



Scheme 1. Proposed mechanism for the Z to E Isomerization of 1,2-Bis(diphenylphosphino)ethene.

is associated with a halide redistribution between two indium atoms to give an  $[InBr_4]^-$  anion and a bis-chelated cation  $[(Z-dppee)_2InBr_2]^+$  with a hexacoordinated indium atom (eq. (4)).

Thus ligand  $Z \rightarrow E$  isomerization is observed neither with InBr<sub>3</sub> nor with InI<sub>3</sub>, and the process appears to be restricted to the strong Lewis acids of aluminium and gallium.

# **Proposed Mechanism**

Formation of an  $\eta^1$ -dppee MX<sub>3</sub> complex like in **2** is proposed as the initial step (Scheme 1). Pentaor hexacoordinated intermediates as in **3**, or in the transition state for the site exchange of the InI<sub>3</sub> unit in **2**, are not likely to be relevant, as the chelating coordination forces the double bond into the Zconfiguration. By contrast, the coordination number of gallium and aluminium in phosphane complexes is largely limited to four [8].

In a qualitative description of the isomerization, the C=C double bond must be turned into a single M. Sigl et al. · 1,2-Bis(diphenylphosphino)ethene





Fig. 1. Molecular structure of **1a** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, hydrogen atoms of the phenyl groups omitted for clarity). Selected bond lengths [Å] and angles [°]: Ga-P 2.4002(8), Ga-Br1 2.3125(5), Ga-Br2 2.2936(6), Ga-Br3 2.3031(5); Br1-Ga-P 100.38(2), Br2-Ga-P 110.57(3), Br3-Ga-P 106.11(3), C1-P-Ga 102.85(9), C111-P-Ga 112.80(10), C211-P-Ga 117.06(10).

bond to allow the rotation to occur. Ylide formation induced by the formal positive charge of the coordinated phosphorus atom appears to be the most obvious model. The differences in catalytic activities are thus correlated with the acceptor properties of the Group 13 trihalides.

It should be noted that reactions of Z-dppee with BrÑnsted acids like trifluoromethanesulfonic or tetrafluoroboric acid also lead to a quaternisation at the phosphorus center, but do not cause isomerization of the C=C double bond upon heating. The reaction may therefore require some direct action of the MX<sub>3</sub> unit at the double bond *via*  $\pi$ -complex formation [9]. There are no experimental observations at hand that could clarify these details.

## **Structural Investigations**

Compound 1 crystallizes in the triclinic space group  $P\bar{I}$  with one formular unit in the unit cell. The complex shows  $C_i$  symmetry with the center of inversion located in the middle of the C=C double bond. The Ga-P distance [2.4008(2) Å] is almost identical with literature values for  $R_3P$ -GaX<sub>3</sub> compounds [8, 10]. The GaBr<sub>3</sub> unit is tilted towards the C=C double bond as shown by the smaller angle C1-P-Ga [102.8(5)°] as compared with C211-P-Ga [117.1(1)°] and C111-P-Ga [112.8(1)°].

Fig. 2. Molecular structure of **2** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: In1-P1 2.5871(12), In1-P2 3.274(1), In1-I1 2.7061(5), In1-I2 2.7420(6), In1-I3 2.7003(5); In1-P1-C1 111.6(2), In1-P1-C111 110.4(2), In1-P1-C121 112.9(2).



Fig. 3. Molecular structure of one of the two independent cations in **3** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, hydrogen atoms of the phenyl groups omitted for clarity). Selected bond lengths [Å] and angles [°]: In1-Br1 2.5985(11) [2.6280(11)], In1-P1 2.696(3) [2.662(3)], In1-P2 2.772(4) [2.770(3)]; Br1-In1-Br1' 180.0 [180.0], P1-In1-P2 77.83(9) [76.23(9)], Br1-In1-P1 92.45(7) [87.59(7)], Br1-In1-P2 90.92(7) [82.84(7)]. The data in brackets refer to the second independent cation.

The crystals of compound **2** are monoclinic, space group  $P2_1/c$  with Z = 4 molecules in the unit cell. Only one phosphorus atom (P1) is coordinated to the metal atom. Quaternisation of P1 causes a formal rehybridisation from  $p^3$  to  $sp^3$ . The increased s character for P1 leads to a shortening of the P-C distances (P1-C average 1.802 Å, P2-C average 1.823 Å) and an opening of the C-P-C angles (C-P1-C average 107.2°, C-P2-C average 102.7°).

The compound with the net composition (Z-dppee)InBr<sub>3</sub> (**3**) was found to have the ionic structure  $[(Z-dppee)_2InBr_2]^+[InBr_4]^-$ . The monoclinic lattice (space group P2<sub>1</sub>/c, Z = 4) is built from two crystallographically independent halves of two cations, one anion and 1/2 CHCl<sub>3</sub>. The indium atoms of the cations (In1, In2) are residing on centers of inversion. The two cations are structurally very similar and do not require a separate discussion. The chelation of the phosphanes to the linear InBr<sub>2</sub><sup>+</sup> unit results in the formation of fivemembered C<sub>2</sub>P<sub>2</sub>In-heterocycles in envelope conformation, with In1 and In2 as spiro-centers. The anion has a standard tetrahedral structure.

#### **Experimental Part**

General: All experiments were carried out routinely in an atmosphere of purified dry nitrogen. Solvents were dried and kept under nitrogen, and glassware was ovendried and filled with nitrogen. All starting materials were commercially available. Gallium and indium trihalides were stored and handled in a glove box.

## $[E-1,2-Bis(diphenylphosphino)ethene](GaBr_3)_2$ (1a)

Gallium tribromide (156 mg, 0.50 mmol) and Z-1,2bis(diphenylphosphino)ethene (100 mg, 0.25 mmol) are reacted in 10 ml of toluene at 80 °C for 1 h. The solvent is distilled off in a vacuum and the residue is recrystallized from chloroform / pentane. Besides traces of a yellow oil, 203 mg (80%) of colorless crystals (m. p. 254°C) are formed. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C):  $\delta$  = 7.06, t, *J*<sub>PH</sub> = 20 Hz, 1H, PCH; 7.52 - 7.90, m, 10H, Ph. - <sup>31</sup>P{<sup>1</sup>H} NMR (v. s.):  $\delta$  = -14.0, br s.

C<sub>26</sub>H<sub>22</sub>Br<sub>6</sub>Ga<sub>2</sub>P<sub>2</sub> (1015.28) Calcd C 30.76 H 2.18%, Found C 30.59 H 2.18%.

The product is the same for reactions with the molar ratio of reactants 1:1, along with E-1,2-Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>. Hydrolysis of **1a** affords E-1,2-Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>.

## [E-1,2-Bis(diphenylphosphino)ethene](GaI<sub>3</sub>)<sub>2</sub> (1b)

As described for **1a** with gallium triiodide (248 mg, 0.55 mmol) and Z-1,2-bis(diphenylphosphino)ethene (109 mg, 0.28 mmol). Yield 264 mg (74 %) of colorless crystals (m. p. 242°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C):  $\delta$  = 7.13,

t,  $J_{PH} = 20$  Hz, 1H, PCH; 7.52 - 7.93, m, 10H, Ph. -  ${}^{31}P\{{}^{1}H\}$  NMR (v. s.):  $\delta = -31.9$ , br s.

 $C_{26}H_{22}I_6Ga_2P_2$  (1297.28)

Calcd C 24.07 H 1.71%, Found C 24.33 H 1.73%.

The product is the same for reactions with the molar ratio of reactants 1:1, along with E-1,2-Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>. Hydrolysis of **1b** affords E-1,2-Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>.

### $[Z-1,2-Bis(diphenylphosphino)ethene]InI_3$ (2)

Indium triiodide (409 mg, 0.825 mmol) is added to a solution of Z-1,2-bis(diphenylphosphino)ethene (326 mg, 0.825 mmol) in 10 ml of dichloromethane. After stirring for 1 h at room temperature the solution is layered with pentane. Yield 688 mg (94%) of pale yellow crystals (m.p. 249°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C):  $\delta$  = 7.21 - 7.59, m, PCH and Ph. - <sup>31</sup>P{<sup>1</sup>H} NMR (v. s.):  $\delta$  = -32.7, br. - <sup>13</sup>C{<sup>1</sup>H} NMR (v. s.):  $\delta$  = 144.2, m, AXX', PCH; 129.0, 131.0, 129.2, 133.4, m, for ipso, ortho, meta, para of Ph.

#### $C_{26}H_{22}InI_3P_2$ (891.94)

Calcd C 35.01 H 2.49%, Found C 34.82 H 2.41%.

Heating of the reaction mixture up to 100 °C for 1 h in toluene leads to the same product.

#### $[Z-1,2-Bis(diphenylphosphino)ethene]_2InBr_2^+ InBr_4^-(3)$

Z-1,2-bis(diphenylphosphino)ethene (127 mg, 0.32 mmol) and InBr<sub>3</sub> (115 mg, 0.32 mmol) are reacted in 10 ml of toluene at room temperature for 2 h. The precipitate is recrystallized from chloroform / pentane. Yield 223 mg (92%) of colorless crystals (m.p. 202°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C):  $\delta$  = 7.26 - 7.71, m, PCH and Ph. - <sup>31</sup>P{<sup>1</sup>H} NMR (v. s.):  $\delta$  = -29.9, br. - <sup>13</sup>C{<sup>1</sup>H} NMR (v. s.):  $\delta$  = 143.6, m, AXX', PCH; 127.5, 133.4, 129.2, 131.4, m, for ipso, ortho, meta, para of Ph.

 $C_{52}H_{44}In_2Br_6P_4$  (1501.88)

Calcd C 41.59 H 2.95%,

Found C 40.27 H 2.78%.

Heating of the reaction mixture up to 100 °C for 1 h in toluene leads to the same product.

## Crystal structure determinations

Specimens of suitable quality and size of compounds **1a**, **2**, and **3** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo- $K_{\alpha}$  radiation,  $\lambda$ (Mo- $K_{\alpha}$ ) = 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 crystals of compounds **1a** and **2**, wereas a decay of 53 %

	1a	$2 \cdot \text{CHCl}_3$	3 · 0.5 CHCl <sub>3</sub>
Crystal data			
Formula	$C_{26}H_{22}Br_6Ga_2P_2$	$C_{27}H_{23}Cl_3I_3InP_2$	$C_{52.5}H_{44.5}Br_6Cl_{1.5}In_2P_4$
Mr	1015.28	1011.26	1561.54
Crystal system	triclinic	monoclinic	monoclinic
Space group	P 1	$P 2_1/c$	$P 2_1/c$
a (Å)	8.836(1)	21.650(3)	21.517(1)
b(A)	9.463(1)	9.849(1)	10.229(1)
<i>c</i> (Å)	11.367(1)	15.883(2)	27.509(1)
$\alpha$ (°)	67.43(1)	90	90
$\beta$ (°)	85.47(1)	101.03(1)	92.79(1)
$\gamma$ (°)	67.99(1)	90	90
$V(\mathbf{A}^3)$	811.36(14)	3324.2(7)	6047.5(8)
$\rho_{\rm calc} ({\rm gcm}^{-3})$	2.078	2.021	1.715
Z	1	4	4
F(000)	480	1896	3012
$\mu(MoK_{\alpha})$ (cm <sup>-1</sup> )	91.62	38.50	49.31
Data collection			
$T(^{\circ}\mathrm{C})$	-80	-79	+26
Scan mode	$\omega$	$\omega$	ω
hkl Range	$-11 \rightarrow 11, -12 \rightarrow 11, -14 \rightarrow 4$	$0 \rightarrow 26, -12 \rightarrow 0, -19 \rightarrow 19$	$-27 \rightarrow 27, -13 \rightarrow 0, 0 \rightarrow 28$
$\sin(\theta/\lambda)_{\rm max} ({\rm A}^{-1})$	0.624	0.62	0.64
Measured reflections	5000	6463	12357
Unique reflections	$3518 [R_{int} = 0.0130]$	6463	$12353 [R_{int} = 0.1384]$
Refls. used for refinement	3496	6078	8738
Absorption correction	psi-scans	DIFABS	DIFABS
Refinement			
Refined parameters Final <i>R</i> values $[I > 2\sigma(I)]$	167	325	596
$R1^{[a]}$	0.0261	0.0332	0.0640
$wR2^{[b]}$	0.0570	0.0799	0.1436
(shift/error) <sub>max</sub>	< 0.001	< 0.001	< 0.001
$\rho_{\text{fin}}(\text{max/min}) (\text{e}\text{\AA}^{-3})$	0.699/-0.453	1.243/-1.149	1.581/-0.852

Table II. Crystal uata, uata conection, and structure remember	Га	Гa	a	h	)	e		II		C	vs	tal	data.	data	col	lection.	and	structure	refineme
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<sup>[a]</sup>  $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|;$  <sup>[b]</sup>  $wR2 = \{[\Sigma w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}; w = 1/[\sigma^2(F_0^2) + (ap)^2 + bp]; p = (F_0^2 + 2F_c^2)/3; a = 0.0246$  (1a), 0.0372 (2 · CHCl<sub>3</sub>), 0.0896 (3 · 0.5 CHCl<sub>3</sub>); b = 0.666 (1a), 14.34 (2 · CHCl<sub>3</sub>), 0.000 (3 · 0.5 CHCl<sub>3</sub>).

was of obtained and corrected for crystals of compound **3**, due to slow decomposition of the compound in the X-ray beam. Lp correction was applied, and data of all compounds were corrected for absorption. The structures were solved by direct methods (SHELXS-86) and completed by full-matrix-least squares techniques against  $F^2$  (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically, except for those of the CHCl<sub>3</sub> molecule in the crystal of compound **3**, which was refined isotropically. Due to its very large thermal parameters, its occupancy was lowered to 50%. All hydrogen atoms with fixed isotropic contributions (U<sub>iso(fix)</sub> = 1.5 x U<sub>eq</sub> of the attached C atom). Information on crystal data,

data collection and structure refinement are summarized in Table II. Important interatomic distances and angles are shown in the corresponding Figure Captions. Anisotropic thermal parameters, tables of interatomic distances and angles, and atomic coordinates have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 410070 (1a), 410069 (2 · CHCl<sub>3</sub>), and 410068 (3 · 0.5 CHCl<sub>3</sub>).

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