

Refinement

Refinement on F^2 $R(F) = 0.044$ $wR(F^2) = 0.090$ $S = 1.227$

5307 reflections

337 parameters

H-atom positions refined

with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$

$$w = 1/[\sigma^2(F_o^2) + (0.0230P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.001$$

$$\Delta\rho_{\text{max}} = 0.158 \text{ e } \text{\AA}^{-3}$$

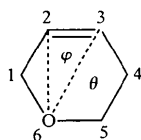
$$\Delta\rho_{\text{min}} = -0.211 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)
Table 2. Selected geometric parameters (\AA , $^\circ$) for (V)

C6—C7	1.513 (2)	C14—C15	1.321 (2)
C7—O18	1.455 (2)	C15—C16	1.470 (2)
C7—C14	1.519 (2)	C16—C17	1.406 (2)
C7—C8	1.524 (2)	C17—O18	1.383 (2)
O18—C7—C6	106.3 (1)	C15—C14—C7	120.4 (1)
O18—C7—C14	109.4 (1)	C14—C15—C16	120.0 (1)
C6—C7—C14	115.5 (1)	C17—C16—C15	116.7 (1)
O18—C7—C8	112.8 (1)	O18—C17—C16	120.6 (1)
C6—C7—C8	101.7 (1)	C17—O18—C7	116.6 (1)
C14—C7—C8	111.1 (1)		
C8—C7—C14—C15	-91.7 (2)	C16—C17—O18—C7	29.6 (2)
C7—C14—C15—C16	-3.3 (2)	C8—C7—O18—C17	78.3 (1)
C14—C15—C16—C22	166.7 (1)	O18—C17—C19—C20	-178.6 (2)
C15—C16—C17—O18	3.1 (2)		

Table 3. Folding angles ($^\circ$) of the pyran ring in compounds (I) to (V)

φ is the dihedral angle (6,2,3)/(2,1,6) and θ is the dihedral angle (6,2,3)/(3,4,6).

	(I)	(II)	(III)	(IV)	(V)
φ	23.1 (2)	22.9 (2)	27.0 (3)	20.7 (2)	28.5 (1)
θ	12.0 (2)	10.0 (2)	15.3 (3)	7.4 (2)	14.6 (1)

Table 4. Photochromic parameters and strain energies of the pyran ring in compounds (I) to (V)

	λ_1 (nm)	A_1	λ_2 (nm)	A_2	λ_3 (nm)	A_3	E_s (kcal mol ⁻¹)†
(I)	436	0.77					9.9
(II)	432	0.84					10.2
(III)	427	1.43	452	1.39	549	0.48	13.1
(IV)	409	0.70	436	0.93	495	1.32	9.8
(V)	447	1.26	534	0.39			12.1

† 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹.

For both compounds, program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL93*.

This work was supported by Russian Fund of Fundamental Investigations (grant N 96-03-32046).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1220). Services for accessing these data are described at the back of the journal.

References

- Aldoshin, S. M., Chuev, I., Utenyshev, A. N., Filipenko, O. S., Lokshin, V., Pozzo, J. L. & Guglielmetti, G. (1996). *Acta Cryst.* **C52**, 1834–1838.
- Aldoshin, S. M., Chuev, I., Utenyshev, A. N., Lokshin, V., Pozzo, J. L., Pèpe, G. & Guglielmetti, G. (1995). *Acta Cryst.* **C51**, 141–143.
- Allinger, N. L. & Young Y. (1977). *Molecular Mechanics MM2 and MMP2 Programs*. Program No. 395. Quantum Chemistry Program Exchange, University of Indiana, Bloomington, USA.
- Miller, J. A., Levoir, P., Fontaine, J. C., Garnier, F. & Dubois, J. F. (1975). *Anal. Chem.* **47**, 29–32.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-3974. Oak Ridge National Laboratory, Tennessee, USA.
- Pozzo, J.-L. (1994). Thesis, Université de la Méditerranée, Marseille, France.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1998). **C54**, 1722–1724

A Water Adduct of Tris(pentafluorophenyl)borane: (C₆F₅)₃B(OH₂)–Dioxane–CH₂Cl₂ (1/1/1)

CHRISTOPH JANIAK,^{a*} LOTHAR BRAUN,^b TOBIAS G. SCHARMANN^b AND FRANK GIRGSDIES^b

^aInstitut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstraße 21, D-79104 Freiburg, Germany, and ^bInstitut für Anorganische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany. E-mail: janiak@uni-freiburg.de

(Received 17 September 1997; accepted 20 May 1998)

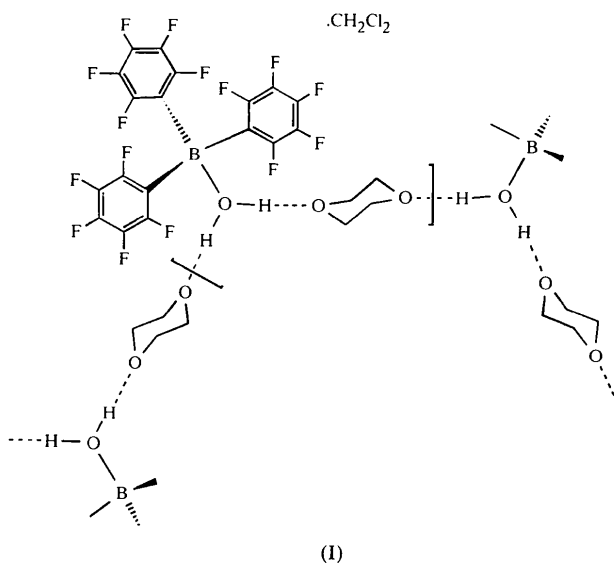
Abstract

The dichloromethane solvate of the 1:1 aquatris(pentafluorophenyl)borane–dioxane adduct, [B(C₆F₅)₃(H₂O)]·C₄H₈O₂·CH₂Cl₂, is a water complex of tris(pentafluorophenyl)borane, which was crystallized from dioxane–methylene chloride solution. The water molecule was carried in either through improperly dried solvent or during the process of crystallization. The structure contains one dioxane and one CH₂Cl₂ molecule per formula unit. Two dioxane molecules form hydrogen bridges to the water molecule and also bridge between two different adduct moieties, so that an infinite chain of borane–water adducts and dioxane molecules is created.

Comment

The organo-Lewis acid tris(pentafluorophenyl)borane, $(C_6F_5)_3B$, is an important activator towards group IV metallocenes in olefin polymerization (Yang *et al.*, 1994; Janiak, 1998). The borane abstracts an alkide or hydride from the metallocene precatalysts, becomes an anion and generates a highly active cationic metallocenium olefin polymerization catalyst. Structural studies of the anionic hydro- or alkyltris(pentafluorophenyl)borate as part of the cation-anion pairs are known, but the structure of the free borane has not been elucidated. We therefore attempted crystallization of the borane by various means. Crystals were eventually grown from methylene chloride which contained 5% by volume of dioxane.

The single-crystal X-ray structure determination indicated, however, that a water adduct of $(C_6F_5)_3B$ had been formed in the course of crystallization. The molecular structure of the title compound, (I), is shown in Fig. 1. The H atoms of the water molecule form hydro-



gen bonds to the dioxane solvent molecules. The dioxane, in turn, bridges between two borane-water adducts, so that a rectangular kinked chain is formed. A molecule of methylene chloride completes the crystal packing. The B—O bond length of 1.565 (3) Å in (I) can be compared to the value of 1.602 (6) Å in the water adduct of Ph_3B (Blake *et al.*, 1988), or to the B—O distance of 1.660 (4) Å in the tetrahydrofuran adduct of Ph_3B (Evans *et al.*, 1996). The shorter bond length in (I) can be ascribed to its increased Lewis acidity, because of the electron-withdrawing fluorophenyl ligands. Even shorter B—O bond lengths are observed in oxy- and hydroxytris(pentafluorophenyl)borates, *e.g.* 1.460 (6) Å in $(C_5Me_5)_2ZrOB(C_6F_5)_3$ (Siedle *et al.*, 1993) and 1.490 (10) Å in $[(C_5Me_5)_2Zr(Me)OH]^+[(C_6F_5)_3BOH]^-$ (Schaefer *et al.*, 1993). Comparative values for the B—O distances in oxytriphenylborate complexes

are 1.59 (3) Å in $(CH_2CH_2N)_3W(O)_2OBPh_3$ (Schreiber *et al.*, 1990) and 1.547 (7) Å in $(acacen)TiOBPh_3$ [$H_2acacen$ = bis(acetylaceton)ethylenediamine; Franceschi *et al.*, 1996]. The B—C bond lengths in (I) are very similar to those found in these other borane and borate complexes. The angles formed between the B—O axis and the phenyl rings are 15.1 (2)° (C11—C16), 46.4 (2)° (C21—C26) and 52.6 (2)° (C31—C36).

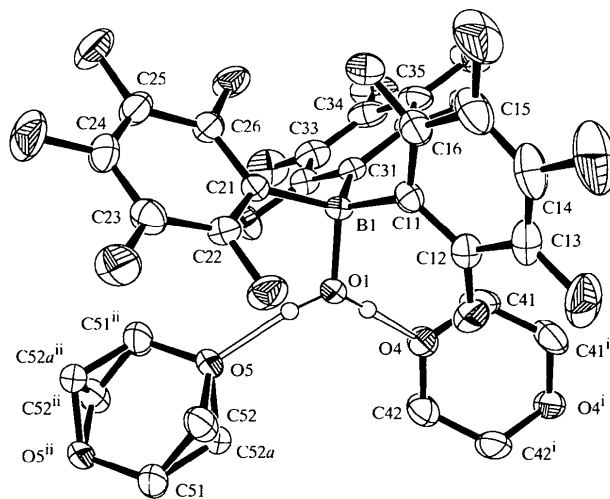


Fig. 1. ORTEP3 (Farrugia, 1997) view of the title compound showing the labelling of the non-H atoms, except the pentafluorophenyl ring oriented to the rear which is not fully labelled because of overlapping graphics [symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, -\frac{1}{2} - y, 1 - z$]. Displacement ellipsoids are shown at the 50% probability level, and the H atoms on the dioxane molecules have been omitted for clarity. One of the dioxane rings is slightly disordered. The numbering of the F atoms is also omitted for clarity: it follows the numbering of the attached C atoms.

Experimental

Synthesis of the title compound was carried out according to the literature method of Massey & Park (1964). Crystallization was achieved by dissolving (I) in dry CH_2Cl_2 , together with 5% by volume of dioxane, and cooling the solution to 203 K. 1H NMR (200 MHz, C_6D_6 , p.p.m.): δ = 3.15 (s, 8H, CH_2 -dioxane), 4.26 (s, 2H, CH_2Cl_2). Note that the chemical shift of CH_2Cl_2 in C_6D_6 is concentration dependent; an NMR measurement of a C_6D_6 sample with a small amount of methylene chloride confirms this assignment. The water protons are not observed, possibly because of their broad resonance due to quadrupolar coupling, and relaxation effects from the B atom (Harris, 1983). ^{13}C NMR (50 MHz, C_6D_6 , p.p.m.): δ = 53.19 (CH_2Cl_2), 66.60 (dioxane), 137.53 (*d, m*-Ph-C), 140.73 (*d, p*-Ph-C), 148.30 (*d, o*-Ph-C), coupling constants $^1J(C, F)$ = 121–123 Hz; again, the boron-bonded *ipso*-phenyl C atom is not observed, because of its broad resonance due to quadrupolar coupling, and relaxation effects from the B atom (Harris, 1983). ^{19}F NMR (188.3 MHz, C_6D_6 , p.p.m.): δ = -127.69 [*dd, o*-F, $J(F, F)$ = 23.8 and 8.5 Hz], -148.26 [*t, p*-F, $J(F, F)$ = 19.6 Hz], -155.92 [*t, m*-F, $J(F, F)$ = 21.7 Hz].

Crystal data

[B(C₆H₅)₃(H₂O)]·C₄H₈O₂·
CH₂Cl₂ $M_r = 703.04$

Monoclinic

 $C2/c$ $a = 17.036 (6) \text{ \AA}$ $b = 16.501 (4) \text{ \AA}$ $c = 19.517 (5) \text{ \AA}$ $\beta = 104.62 (2)^\circ$ $V = 5309 (3) \text{ \AA}^3$ $Z = 8$ $D_x = 1.759 \text{ Mg m}^{-3}$ D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer $\omega/2\theta$ scans

Absorption correction: none

12 129 measured reflections

6077 independent reflections

3197 reflections with

 $I > 2\sigma(I)$ Mo $K\alpha$ radiation $\lambda = 0.71069 \text{ \AA}$ Cell parameters from 25
reflections $\theta = 9.9\text{--}11.9^\circ$ $\mu = 0.377 \text{ mm}^{-1}$ $T = 160 (2) \text{ K}$

Irregular platelet

 $0.33 \times 0.30 \times 0.21 \text{ mm}$

Colourless

 $R_{\text{int}} = 0.069$ $\theta_{\text{max}} = 27.47^\circ$ $h = -22 \rightarrow 22$ $k = 0 \rightarrow 21$ $l = -25 \rightarrow 25$

3 standard reflections

every 200 reflections

intensity decay: none

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.046$ $wR(F^2) = 0.124$ $S = 1.003$

6077 reflections

431 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 3.0089P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.421 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.306 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for
Crystallography (Vol. C)Table 1. Selected geometric parameters (\AA , $^\circ$)

B1—O1	1.565 (3)	O1—H12	0.96 (4)
B1—C11	1.633 (4)	C11—C1	1.763 (4)
B1—C31	1.633 (4)	C12—C1	1.729 (4)
B1—C21	1.635 (4)	O5—H11	1.72 (4)
O1—H11	0.86 (4)	O4—H12	1.64 (4)
O1—B1—C11	107.8 (2)	C31—B1—C21	114.2 (2)
O1—B1—C31	105.8 (2)	B1—O1—H11	119 (3)
C11—B1—C31	115.5 (2)	B1—O1—H12	118 (2)
O1—B1—C21	104.4 (2)	H11—O1—H12	114 (4)
C11—B1—C21	108.3 (2)		

H atoms were refined with fixed displacement parameters. The H atoms on the disordered dioxane molecule were calculated.

Data collection: *CAD-4/PC* (Kretschmar, 1994). Cell refinement: *CAD-4/PC*. Data reduction: *XCAD4* (Harms, 1996). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP3* (Farrugia, 1997).

The authors thank the DFG, the Fonds der Chemischen Industrie and the graduate college in Synthetic, Mechanistic and Reaction Engineering Aspects of Metal Catalysts at the TU Berlin, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1004). Services for accessing these data are described at the back of the journal.

References

- Blake, A. J., Greig, J. A. & Schröder, M. (1988). *J. Chem. Soc. Dalton Trans.* pp. 2645–2647.
- Evans, W. J., Shreeve, J. L. & Ziller, J. W. (1996). *Acta Cryst.* **C52**, 2571–2573.
- Farrugia, L. J. (1997). *ORTEP3 for Windows*. Version 1.0.1.β. University of Glasgow, Scotland.
- Franceschi, F., Gallo, E., Solari, E., Floriani, C., Chiesi-Villa, A., Rizzoli, C., Re, N. & Sgamellotti, A. (1996). *Chem. Eur. J.* **2**, 1466–1476.
- Harms, K. (1996). *XCAD4. Program for Reduction of CAD-4 Diffractometer Data*. University of Marburg, Germany.
- Harris, R. K. (1983). *Nuclear Magnetic Resonance Spectroscopy*, pp. 138–141. London: Pitman.
- Janiak, C. (1998). *Metallocene Catalysts for Olefin Polymerization*, in *Metallocenes*, edited by A. Togni & R. L. Halterman. Weinheim: Wiley-VCH. In the press.
- Kretschmar, M. (1994). *CAD-4/PC. Program for Data Collection and Cell Refinement*. Version 1.5c. University of Tübingen, Germany.
- Massey, A. G. & Park, A. J. (1964). *J. Organomet. Chem.* **2**, 245–247.
- Schaefer, W. P., Quan, R. W. & Bercau, J. E. (1993). *Acta Cryst.* **C49**, 878–881.
- Schreiber, P., Wieghardt, K., Nuber, B. & Weiss, J. (1990). *Z. Naturforsch. Teil B*, **45**, 619–628.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siedle, A. R., Newmark, R. A., Lamanna, W. M. & Huffman, J. C. (1993). *Organometallics*, **12**, 1491–1492.
- Yang, X., Stern, C. L. & Marks, T. J. (1994). *J. Am. Chem. Soc.* **116**, 10015–10031.

Acta Cryst. (1998). **C54**, 1724–1727

1,5-Diphenylbicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic Anhydride and 1,5-Diphenylbicyclo[2.2.1]hept-5-ene-*exo*-2,*exo*-3-dicarboxylic Anhydride

AARNE PAJUNEN^a AND MARIITTA KOKKO^b

^aLaboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, Box 55, FIN-00014 University of Helsinki, Finland, and ^bLaboratory of Organic Chemistry, Department of Chemistry, University of Helsinki, Box 55, FIN-00014 University of Helsinki, Finland. E-mail: aarne.pajunen@helsinki.fi

(Received 6 April 1998; accepted 19 June 1998)

Abstract

The change of the anhydride group with respect to the cyclopentene ring in the *endo* and *exo* isomers of C₂₁H₁₆O₃ is reflected in the conformation of the phenyl