= 0.93, C—H(methyl) = 0.96, C—H(secondary) = 0.97 or C—H(tertiary) = 0.98 Å, respectively. The methyl group was allowed to rotate abouts its local threefold axis.

Data collection: *SDP* (Enraf–Nonius, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1036). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Product of Catalysed Diboration of Bis(4-methoxyphenyl)ethyne by Bis(pinacolato-*O*,*O*′)diboron

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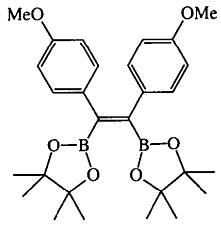
Abstract

The title compound, (*Z*)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-bis(4-methoxyphenyl)ethene, $C_{28}H_{38}B_2O_6$, has a *cis* arrangement of two boronate ester substituents and two 4-methoxyphenyl substituents on its central C═C double bond, which shows a slight twist of *ca* 8.5°. All four substituents are rotated considerably out of the alkene plane to reduce steric hindrance. The BO_2C_2 five-membered rings have a twist conformation.

Comment

We and others have recently reported the catalysed addition of B—B bonds to alkenes (Baker, Nguyen, Marder & Westcott, 1995) and alkynes (Ishiyama, Matsuda, Miyaura & Suzuki, 1993; Iverson & Smith, 1995; Lesley *et al.*, 1996), and have prepared and structurally characterized several platinum(II)–bis(phosphine)–bis(boryl) complexes formed by oxidative addition of the B—B bonds to bisphosphine Pt(0) centres. Initial studies (Ishiyama *et al.*, 1993) of the addition of bis(pinacolato-*O*,*O*′)diboron, B_2pin_2, to alkynes suggested that this results in *cis*-alkene-1,2-bis(boronate esters) on the basis of NMR measurements, and we have confirmed this stereochemistry by X-ray crystallography for the addition of bis(benzene-1,2-diolato)diboron [or bis(catecholato-*O*,*O*′)diboron, B_2cat_2] to internal and terminal alkynes as well as to 1,3-diynes (Lesley *et al.*, 1996). We also found that reactions using B_2pin_2 were slower than those using B_2cat_2.



(I)

We report here the structure of the product (I) of the addition of B_2pin_2 to the symmetrical internal alkyne bis(4-methoxyphenyl)ethyne, which confirms that this addition also gives *cis*-boronate ester substituents (Fig. 1.) The geometry of the central C_4B_2 part of the molecule is essentially the same as for the B_2cat_2 adducts. There is a small twist about the C═C double bond, as measured by the C—C—C—C and B—C—C—B torsion angles of 8.0 (2) and 9.0 (2)°, respectively. The central C_4B_2 mean plane [r.m.s. deviation 0.067 (2) Å] has dihedral angles with the two aromatic rings [r.m.s. deviations 0.006 (2) and 0.005 (2) Å] of 44.6 (1) and 51.4 (1)°, and with the two CBO_2 boron coordination mean planes [r.m.s. deviations 0.027 (2) and 0.006 (2) Å] of 66.0 (1) and 22.1 (1)°, to avoid steric congestion.

The two BO_2C_2 five-membered boronate ester rings have very similar twist conformations, each with one C atom on one side [by 0.235 (2) and 0.269 (2) Å] and one on the other side [by 0.257 (2) and 0.213 (2) Å] of

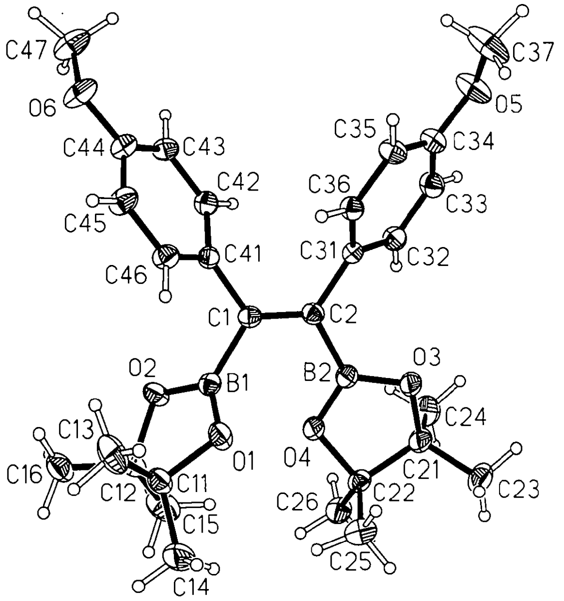


Fig. 1. The molecular structure with atom labels and 50% probability ellipsoids for non-H atoms.

the BO_2 plane, and with O—C—C—O torsion angles of −29.27 (12) and +28.68 (12)°. In 67 XO_2C_2 rings for pinacol derivatives found in the Cambridge Structural Database (Allen & Kennard, 1993), the majority (63) have O—C—C—O torsion angles between 10 and 50° (ignoring the sign), with 54 above 30°; interestingly, the four almost planar rings include those of the starting material B_2pin_2 itself (Nöth, 1984), with a torsion angle of only 1.6 (3)°; this conformation, together with other details of the ring geometry such as the B—O bond lengths [mean value 1.324 (4) Å] and angles at B and O atoms [111.1 (2) and mean value 111.8 (3)°, respectively], is modified substantially in the adduct reported here.

The structure has no notably short intermolecular contacts.

Experimental

The compound was prepared by platinum-catalysed addition of bis(pinacolato-*O*,*O*′)diboron (B_2pin_2) to bis(4-methoxyphenyl)ethyne, as described by Lesley *et al.* (1996). Crystals were obtained by diffusion of a layer of hexane into a solution in $CDCl_3$.

Crystal data

$C_{28}H_{38}B_2O_6$
$M_r = 492.20$
Orthorhombic
*Fdd*2
$a = 20.7331\ (15)$ Å
$b = 35.970\ (3)$ Å
$c = 14.6595\ (11)$ Å
$V = 10932.6\ (14)$ Å^3
$Z = 16$
$D_x = 1.196$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 12021 reflections
$\theta = 2.04$–28.30°
$\mu = 0.081$ mm^{-1}
$T = 160\ (2)$ K
Block
0.81 × 0.34 × 0.30 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
Sets of exposures each taken over 0.3° ω rotation
Absorption correction: none
16566 measured reflections
6168 independent reflections

5710 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0237$
$\theta_{\rm max} = 28.47°$
$h = -11 \rightarrow 27$
$k = -48 \rightarrow 47$
$l = -19 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0304$
$wR(F^2) = 0.0771$
$S = 1.051$
6166 reflections
336 parameters
H atoms riding (see text)
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 7.6635P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.192$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.142$ e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1994)
Extinction coefficient: 0.00034 (3)
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)*

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

	x	y	z	$U_{\rm eq}$
C1	0.25799 (6)	0.07871 (3)	−0.10279 (8)	0.0210 (2)
C2	0.20038 (6)	0.07264 (3)	−0.06136 (8)	0.0212 (2)
B1	0.28810 (7)	0.11852 (4)	−0.11922 (10)	0.0213 (3)
O1	0.30919 (5)	0.14082 (3)	−0.04992 (6)	0.0269 (2)
O2	0.30465 (5)	0.13137 (2)	−0.20404 (6)	0.0268 (2)
C11	0.35269 (6)	0.16810 (4)	−0.09075 (9)	0.0269 (3)
C12	0.32948 (7)	0.16908 (3)	−0.19182 (9)	0.0255 (3)
C13	0.42054 (7)	0.15260 (5)	−0.07916 (12)	0.0401 (4)
C14	0.34686 (9)	0.20470 (5)	−0.04029 (13)	0.0464 (4)
C15	0.27330 (8)	0.19513 (4)	−0.20799 (13)	0.0445 (4)
C16	0.38253 (8)	0.17645 (4)	−0.26088 (10)	0.0360 (3)
B2	0.15542 (7)	0.10643 (4)	−0.03991 (10)	0.0227 (3)
O3	0.10612 (4)	0.10541 (3)	0.02182 (7)	0.0292 (2)
O4	0.16052 (4)	0.13983 (2)	−0.08443 (6)	0.0242 (2)
C21	0.06683 (6)	0.13862 (4)	0.00625 (9)	0.0273 (3)
C22	0.11614 (6)	0.16554 (3)	−0.03893 (9)	0.0249 (3)
C23	0.04023 (9)	0.15157 (4)	0.09749 (11)	0.0403 (4)
C24	0.01247 (7)	0.12697 (5)	−0.05741 (12)	0.0396 (3)
C25	0.15524 (7)	0.18792 (4)	0.02954 (11)	0.0364 (3)
C26	0.08753 (7)	0.19101 (4)	−0.11113 (10)	0.0321 (3)
C31	0.17688 (6)	0.03507 (3)	−0.03290 (8)	0.0212 (2)
C32	0.11197 (6)	0.02481 (4)	−0.04313 (10)	0.0255 (3)
C33	0.08971 (6)	−0.00924 (4)	−0.01389 (10)	0.0288 (3)
C34	0.13082 (7)	−0.03400 (4)	0.02952 (10)	0.0271 (3)
C35	0.19509 (6)	−0.02450 (4)	0.04159 (9)	0.0265 (3)
C36	0.21731 (6)	0.00950 (3)	0.00971 (9)	0.0235 (2)
O5	0.10389 (5)	−0.06676 (3)	0.05717 (8)	0.0415 (3)
C37	0.14093 (10)	−0.08933 (5)	0.11765 (15)	0.0566 (5)
C41	0.30160 (6)	0.04844 (3)	−0.13587 (8)	0.0209 (2)
C42	0.28013 (6)	0.01981 (4)	−0.19211 (9)	0.0248 (3)
C43	0.32174 (6)	−0.00708 (4)	−0.22633 (9)	0.0258 (3)
C44	0.38664 (6)	−0.00566 (4)	−0.20345 (9)	0.0269 (3)
C45	0.40923 (6)	0.02274 (4)	−0.14781 (10)	0.0316 (3)
C46	0.36743 (6)	0.04945 (4)	−0.11542 (9)	0.0267 (3)
O6	0.43204 (5)	−0.03093 (3)	−0.23116 (8)	0.0392 (3)
C47	0.41408 (9)	−0.05695 (5)	−0.29965 (13)	0.0453 (4)

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

C1—C2	1.358 (2)	B1—O1	1.366 (2)
C1—C41	1.496 (2)	B1—O2	1.370 (2)
C1—B1	1.580 (2)	B2—O3	1.366 (2)
C2—C31	1.496 (2)	B2—O4	1.371 (2)
C2—B2	1.564 (2)		
C2—C1—C41	124.04 (11)	O2—B1—C1	122.88 (11)
C2—C1—B1	124.15 (11)	B1—O1—C11	106.70 (10)
C41—C1—B1	111.79 (10)	B1—O2—C12	106.86 (10)
C1—C2—C31	123.82 (11)	O3—B2—O4	113.38 (11)
C1—C2—B2	119.30 (11)	O3—B2—C2	123.94 (11)
C31—C2—B2	116.87 (10)	O4—B2—C2	122.64 (11)
O1—B1—O2	113.35 (11)	B2—O3—C21	106.92 (10)
O1—B1—C1	123.03 (11)	B2—O4—C22	106.74 (10)

The data collection nominally covered more than a hemisphere of reciprocal space. Coverage of the unique set is virtually complete to at least 26.4° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections.

H atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. The combination of X-ray wavelength and elements present in the compound does not permit a reliable determination of the absolute structure (Flack, 1983).

Data collection: *SMART* (Siemens, 1995). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* 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 IUCr (Reference: AB1368). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Products of Catalysed Diboration of Bis(*p*-tolyl)ethyne and of 4-Cyanophenylethyne by Bis(catecholato-*O*,*O*′)diboron

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Abstract

Both (*Z*)-1,2-bis(1,3,2-benzodioxaborolan-2-yl)-1,2-bis(4-methylphenyl)ethene [(I), $C_{28}H_{22}B_2O_4$] and (*Z*)-4-[1,2-bis(1,3,2-benzodioxaborolan-2-yl)vinyl]benzonitrile [(II), $C_{21}H_{13}B_2NO_4$] have a *cis* arrangement of two boronate ester substituents on a C═C double bond, which shows a slight twist to relieve steric crowding of the substituents. The interplay of steric and electronic factors results in approximate coplanarity of only one substituent with the alkene unit in (I), while this is achieved for two mutually *trans* substituents in the less crowded (II). A consistent pattern of bonding and conformational geometry is found for a series of related alkenes with boronate ester substituents. The catecholboronate group shows almost invariant geometry across a range of compounds, with a slight but probably real lengthening of the B—O bonds on coordination to transition metals.

Comment

The addition of B—B bonds to alkynes is catalyzed by platinum bis(phosphine) complexes and leads to *cis*-alkene-1,2-bis(boronate esters) (Ishiyama, Matsuda, Miyaura & Suzuki, 1993; Iverson & Smith, 1995; Lesley *et al.*, 1996; Ishiyama *et al.*, 1996). We have reported previously the structure of one product of addition of bis(pinacolato-*O*,*O*′)diboron, B_2pin_2, to a symmetrical alkyne (Clegg, Scott, Lesley, Marder & Norman, 1996) and of representative products of addition of bis(catecholato-*O*,*O*′)diboron, B_2cat_2, to an internal alkyne, a terminal alkyne, and a 1,3-diyne (Lesley *et al.*, 1996). We report here the structures of two further adducts of B_2cat_2 with alkynes, with an analysis of the whole series of related structures and other molecules containing the Bcat unit, including the starting material B_2cat_2 itself (Nguyen *et al.*, 1994).

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