

Analysis of geometric parameters and packing considerations for triphenylboroxine derivatives, with tris(pentafluorophenyl)boroxine as an example

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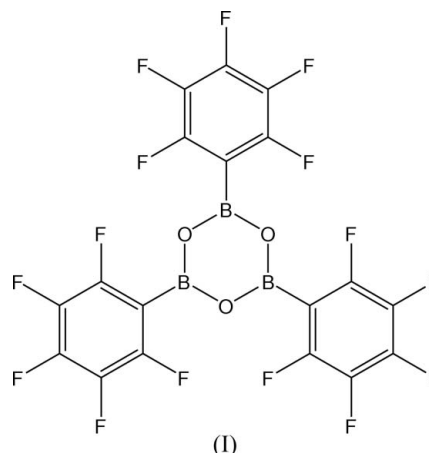
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Molecules of the title compound [systematic name: 2,4,6-(pentafluorophenyl)-1,3,5,2,4,6-trioxatriborinane], $C_{18}B_3F_{15}O_3$, are located on crystallographic twofold rotation axes which run through the boroxine and one of the pentafluorophenyl rings. The boroxine ring (r.m.s. deviation = 0.027 Å) and the pentafluorophenyl rings (r.m.s. deviations = 0.004 and 0.001 Å) are essentially planar. The dihedral angles between the boroxine and the two symmetry-independent benzene rings are 8.64 (10) and 8.74 (12)°. The two benzene rings are mutually coparallel [dihedral angle = 0.80 (11)°]. The packing shows planes of molecules parallel to $(\bar{2}01)$, with an interplanar spacing of 2.99 Å. Within these planes, all the molecules are oriented in the same direction, whereas in neighbouring planes the direction is inverted. Short B...F contacts of 3.040 (2) and 3.1624 (12) Å occur between planes. The geometric parameters of the boroxine ring in the title compound agree well with those of comparable boroxine structures, while the packing reveals some striking similarities and differences.

Comment

It has been known for decades that the Si—Si bond in halo-substituted disilanes can be cleaved in the presence of a Lewis base (Meyer-Wegner *et al.*, 2011). The reactivity of Si_2Cl_6 has been studied mostly with a focus on its behaviour towards neutral N and P donors, yet some reactions of Si_2Cl_6 with anionic nucleophiles have also been described (Meyer-Wegner *et al.*, 2009). Recently, we have discovered that the reaction of Si_2Cl_6 with two equivalents of $Na[Si^tBu_3]$ (Lerner, 2005) leads to several products, such as neopentasilane Si_5Cl_{12} and the tetrasilatetrahedrane $Si_4(Si^tBu_3)_4$ (Meyer-Wegner *et al.*, 2009), but no substitution product [$(^tBu_3Si)SiCl_2SiCl_2(Si^tBu_3)$; Bolte & Lerner 2011] was formed thereby. The title boroxine, (I), was obtained by the reaction of the Lewis acid tris(penta-

fluorophenyl)borane monohydrate with Si_2Cl_6 . In this study, we describe the molecular and crystal structure of (I). Single crystals were isolated from the reaction solution on cooling from 453 K to room temperature.



Boronic acids, $RB(OH)_2$ (R = alkyl or aryl), can be readily converted to the corresponding boroxines, $(RBO)_3$. Although the B centres in boroxines possess a higher Lewis acidity than the C atoms in arenes, X-ray structure analysis provides evidence for the existence of a π -ring system in boroxines. Owing to significant differences in both the steric and electronic properties of the ligands of boroxines, different crystal-packing patterns have been found in their crystal structures (Boese *et al.*, 1987).

The molecule of (I) (Fig. 1) is located on a crystallographic twofold rotation axis running through the boroxine ring and one of the pentafluorophenyl rings. The boroxine ring (r.m.s. deviation = 0.027 Å) and pentafluorophenyl rings (r.m.s. deviations = 0.004 and 0.001 Å) are essentially planar. The dihedral angles between the boroxine ring and the two

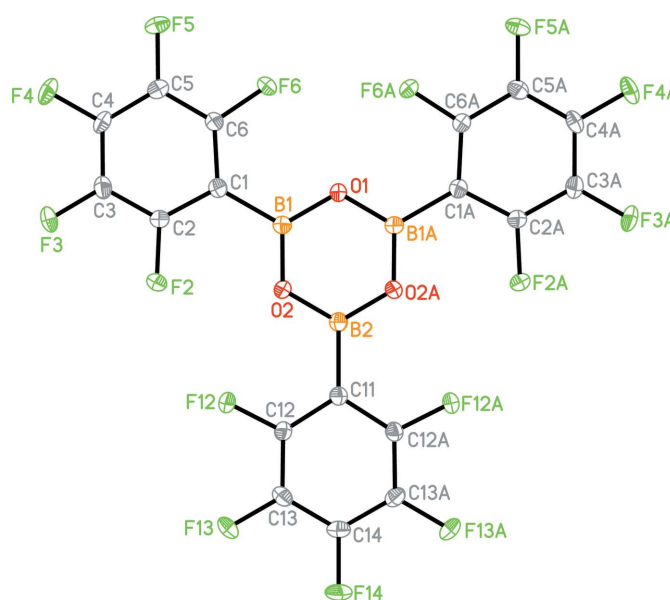


Figure 1

A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (A) $-x, y, -z + \frac{1}{2}$]

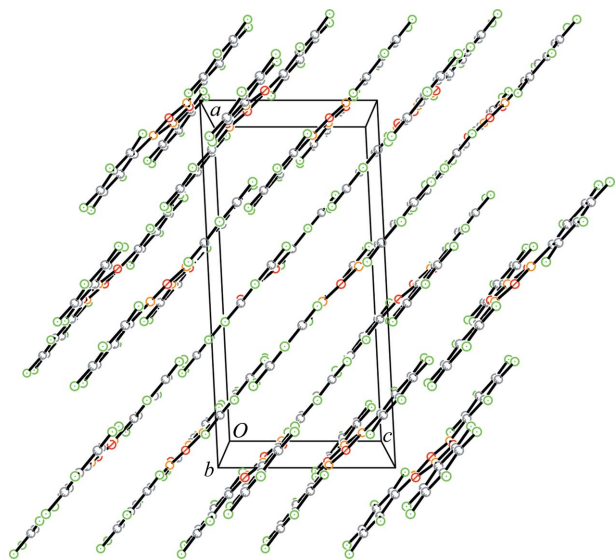


Figure 2
A packing diagram for (I), viewed in the *ac* plane.

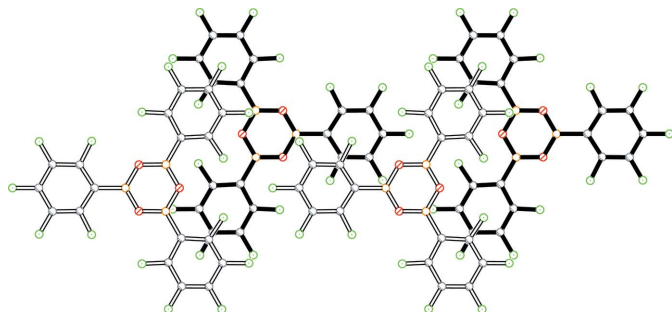


Figure 3
A partial packing diagram for (I), showing two coparallel planes. The molecules in one plane are drawn with full bonds and those in the other plane with open bonds. The view direction is onto the (201) plane. Cell boundaries have been omitted for clarity.

symmetry-independent benzene rings are 8.64 (10) and 8.74 (12)°. The two benzene rings are mutually coparallel [dihedral angle = 0.80 (11)°]. The packing (Fig. 2) shows planes of molecules parallel to (201) with an interplanar spacing of 2.99 Å. Within each plane, all the molecules are oriented in the same direction, whereas in neighbouring planes the direction is inverted (Fig. 3). There is no π - π stacking but it is noteworthy that short B...F distances occur between two planes [$B1 \cdots F5^{ii} = 3.040$ (2) Å and $B2 \cdots F13^{iii} = 3.1624$ (12) Å; symmetry codes: (ii) $x, -y + 1, z - \frac{1}{2}$; (iii) $x, -y + 2, z - \frac{1}{2}$]. The F atom is located almost directly over the B atom (Fig. 3).

Boroxines with alkyl substituents, such as (EtBO)₃, form columns in their crystal structures in which the boroxine rings stack above each other, with each B atom being surrounded by the O atoms of the two neighbouring layers (Fig. 4) (Beckett *et al.*, 1997). Between these layers there are short intermolecular B...O contacts of 3.462 Å. In contrast, boroxines with aryl substituents tend to form, in most cases, a layer structure in the solid state in which the boroxine rings are located between two arene rings of neighbouring layers (Fig. 5) (Brock *et al.*, 1987). Generally, X-ray structure analyses of boroxines provide

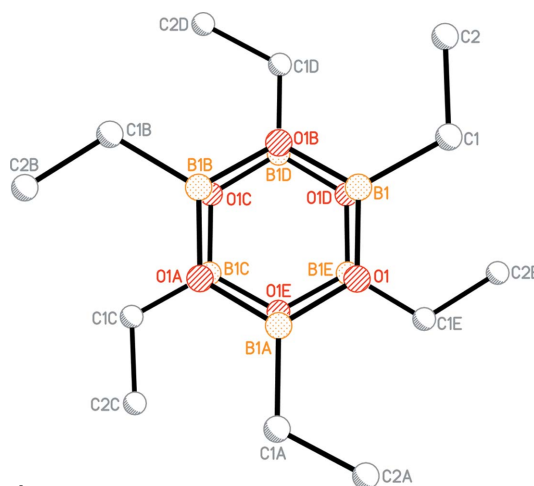


Figure 4
A partial packing diagram for triethylboroxine (Beckett *et al.*, 1997), viewed perpendicular to the boroxine ring. H atoms have been omitted for clarity. [Symmetry codes: (A) $-x + y + 2, -x + 1, z$; (B) $-y + 1, x - y - 1, z$; (C) $-x + 2, -y, -z$; (D) $x - y, x - 1, -z$; (E) $y + 1, -x + y + 1, -z$.]

evidence for the existence of a π -ring system (Haberecht *et al.*, 2005).

In order to compare the molecular and crystal structures of (I) with those of similar compounds, a Cambridge Structural Database (CSD, Version 5.33 of November 2011 plus one update; Allen, 2002) substructure search was undertaken for boroxine rings with each B atom connected to a benzene ring and yielded 17 hits. All rings are essentially planar, with a mean absolute B—O—B—O torsion angle of 3 (2)° and a maximum absolute torsion angle of 11.8°. The mean B—O

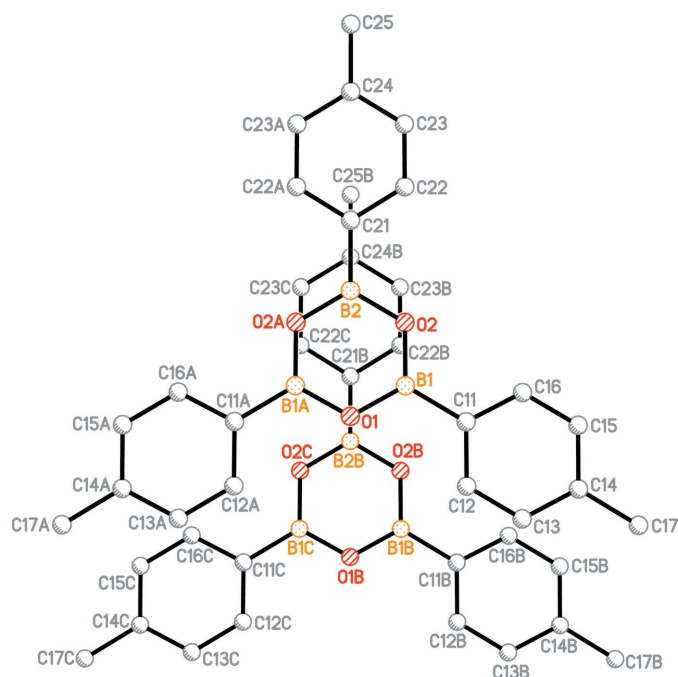


Figure 5
A partial packing diagram for tris(*p*-tolyl)boroxine (Brock *et al.*, 1987), viewed perpendicular to the boroxine ring. H atoms have been omitted for clarity. [Symmetry codes: (A) $-x, y, z$; (B) $x, y, z + 1$; (C) $-x, y, z + 1$.]

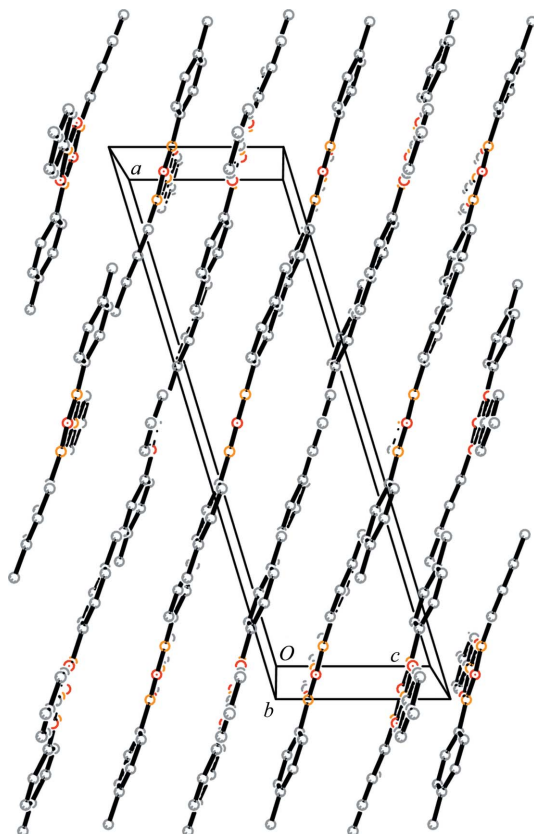


Figure 6
A packing diagram for the monoclinic form of tris(*p*-tolyl)boroxine (NIBGOU; Beckett *et al.*, 1997), viewed in the *ac* plane. H atoms have been omitted for clarity.

distance over all six B—O bonds in all hits was 1.379 (7) Å. The mean O—B—O angle is 118.4 (9)°, whereas the mean B—O—B angle is 121.5 (9)°.

In (I), the mean absolute B—O—B—O torsion angle is 4 (2)°, with a maximum value of -6.5 (2)° for B2—O2—B1—O1. The B—O distances range from 1.364 (2) Å for B1—O2 to 1.3713 (19) Å for B1—O1. In contrast with the structures retrieved from the database, the B—O—B and O—B—O angles in (I) have almost the same values [B1—O1—B1ⁱ = 119.82 (18)°, B1—O2—B2 = 120.13 (14)°, O2—B1—O1 = 119.81 (14)° and O2—B2—O2ⁱ = 119.8 (2)°; symmetry code: (i) $-x, y, -z + \frac{1}{2}$].

Four compounds from the database search are very similar to (I) and merit further investigation. It is remarkable that neither triphenylboroxine [FIPDOX (Boese *et al.*, 1987), FIPDOX01 (Brock *et al.*, 1987) and FIPDOX02 (Bolte, 2004)], 2,4,6-tris(4-bromophenyl)boroxine [LUKKAD (Avent *et al.*, 2002), LUKKAD01 (Jones & Zerbe, 2004) and LUKKAD02 (Bhuvanesh *et al.*, 2005)], tris(*p*-tolyl)boroxine [NIBGOU (Beckett *et al.*, 1997) and NIBGOU01 (Haberecht *et al.*, 2005)] nor 1,3,5-trimesitylboroxine [SOKLAF (Neumüller & Gahlmann, 1991), SOKLAF01 (Anulewicz-Ostrowska *et al.*, 2000) and SOKLAF02 (Franz *et al.*, 2009)] is isomorphous with (I).

1,3,5-Trimesitylboroxine (SOKLAF) has a completely different packing pattern from (I), which is most probably due to the fact that the mesityl residues are significantly twisted

out of the plane of the boroxine ring (35.8 and 40.6°). As a result, this structure will not be discussed in detail.

Although triphenylboroxine (FIPDOX) features a rather planar molecule (r.m.s. deviation for all non-H atoms = 0.178 Å), the crystal packing shows neither planes of coparallel molecules nor any π -stacking. There are only some weak C—H $\cdots\pi$ contacts in the range 2.93–3.44 Å. The planar boroxine ring (r.m.s. deviation = 0.035 Å) forms dihedral angles of 6.5, 11.9 and 11.6° with the attached phenyl rings.

Tris(*p*-tolyl)boroxine (NIBGOU) crystallizes, like (I), in the monoclinic space group *C2/c* but with rather different cell parameters [$a = 22.591$ (2), $b = 13.269$ (4), $c = 6.839$ (1) Å, $\beta = 106.82$ (2)° and $V = 1962.3$ Å³]. As in (I), molecules of NIBGOU are located on a crystallographic twofold rotation axis. The planar boroxine ring (r.m.s. deviation for all non-H atoms = 0.001 Å) forms dihedral angles of 9.3 and 1.9° with the attached benzene rings; the r.m.s. deviation for all non-H atoms is 0.062 Å. Nevertheless, the packing of the molecules is, on the one hand, similar to that in (I), *i.e.* the molecules form layers parallel to $(\bar{2}01)$, with an interplanar spacing of 3.25 Å (Fig. 6). The difference in the packing pattern, on the other hand, is that in NIBGOU the boroxine rings are stacked above a benzene ring (Fig. 5). This kind of stacking of rings is not observed in (I), where B \cdots F contacts are found.

NIBGOU01 is a polymorph of NIBGOU. It crystallizes in the orthorhombic space group *Pmn*2₁ with the molecules located on a crystallographic mirror plane. The boroxine ring is again planar (r.m.s. deviation = 0.019 Å) and forms dihedral

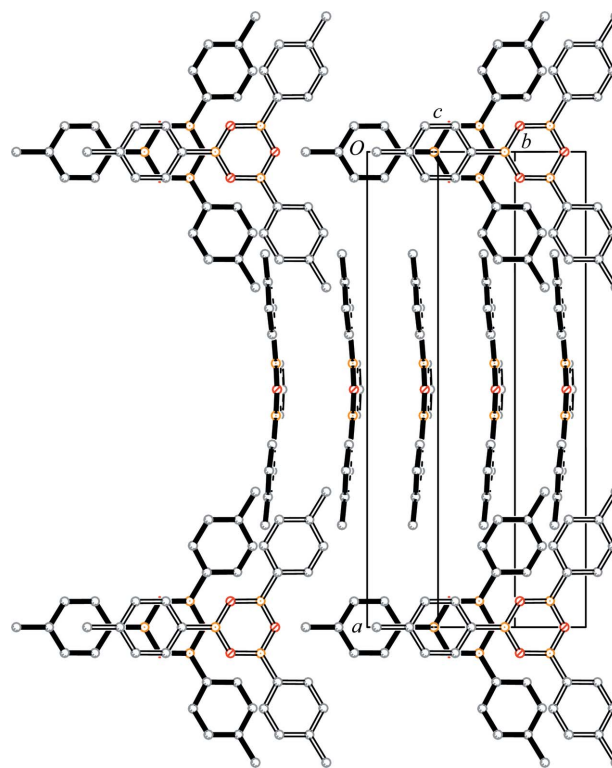


Figure 7
A packing diagram for the orthorhombic form of tris(*p*-tolyl)boroxine (NIBGOU01; Haberecht *et al.*, 2005), viewed in the $(0\bar{2}1)$ plane. H atoms have been omitted for clarity.

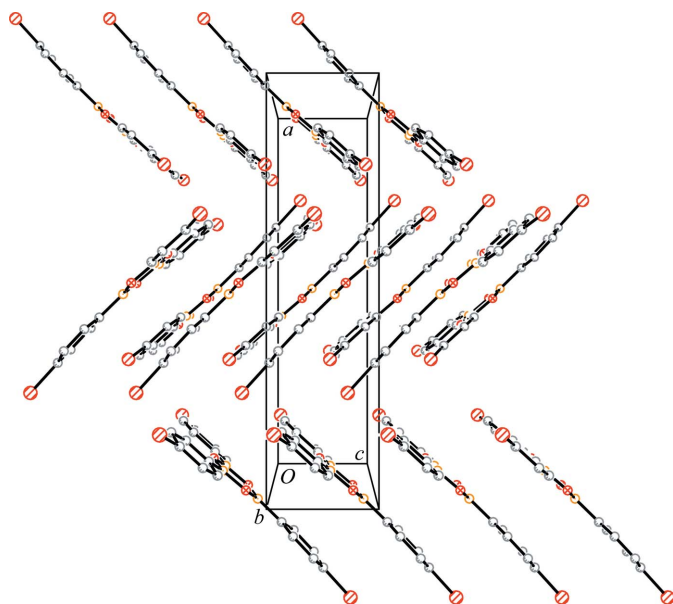


Figure 8
A packing diagram for tris(*p*-bromophenyl)boroxine (LUKKAD; Avent *et al.*, 2002), viewed in the *ac* plane. H atoms have been omitted for clarity.

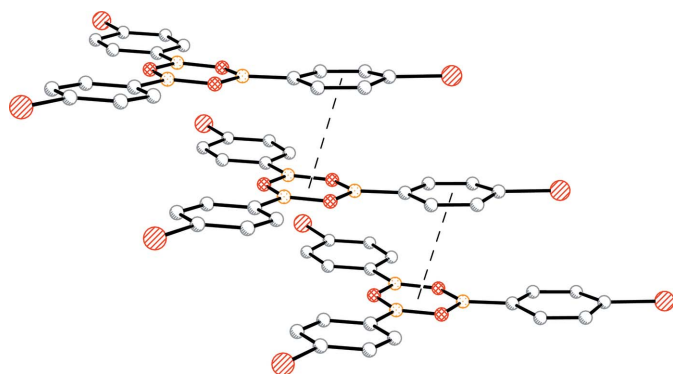


Figure 9
A partial packing diagram for tris(*p*-bromophenyl)boroxine (LUKKAD; Avent *et al.*, 2002). H atoms have been omitted for clarity. Centroid-centroid distances are drawn as dashed lines.

angles of 5.7 and 4.2° with the attached benzene rings. Again, the molecules form planes with boroxine rings stacked above benzene rings (Fig. 7), but there are different layers of molecules parallel to (021) and (021̄). The dihedral angle between the layers is 86.1° and the interplanar spacing is 3.33 Å.

The molecules of 2,4,6-tris(4-bromophenyl)boroxine (LUKKAD) show crystallographic mirror symmetry. The boroxine ring is planar (r.m.s. deviation = 0.016 Å) and makes dihedral angles of 2.9 and 5.4° with the benzene rings. The packing of the molecules resembles a herringbone pattern, with molecules in planes parallel to (401) and (401̄) (Fig. 8). The dihedral angle between these planes is 87.1° and the interplanar spacing is 3.37 Å. In this case, stacking of boroxine with benzene rings is observed (Fig. 9). The centroid-centroid distance is 3.51 Å.

In conclusion, it can be said that aryl-substituted boroxine rings tend to adopt a planar molecular structure. The aryl rings are only twisted out of the boroxine plane if bulky substituents in the *ortho* position of the aryl substituents avoid coplanarity

of the aryl and boroxine rings. The phenyl-, *p*-bromophenyl-, tolyl- and pentafluorophenyl-substituted boroxines are located on a crystallographic symmetry element, either on a mirror plane or on a twofold rotation axis. Whereas the crystal packing of triphenylboroxine does not reveal any stacking, the molecules of *p*-bromophenyl-, tolyl- and pentafluorophenylboroxine show a layer structure. However, the kind of stacking is different depending on the substitution pattern of the boroxine ring. In *p*-bromophenyl- and tolylboroxine, the boroxine rings are stacked above the benzene rings, whereas in pentafluorophenylboroxine no stacks of rings occur but short B⋯F interactions are found. This is the reason for the different packing pattern of (I) compared with the other boroxines discussed. On the other hand, the alkyl-substituted compound triethylboroxine shows perfect boroxine–boroxine stacks.

Experimental

Tris(pentafluorophenyl)borane monohydrate (0.32 g, 0.60 mmol) and hexachlorodisilane (0.1 ml, 0.57 mmol) were dissolved in C₆D₆ (0.5 ml). The reaction mixture was heated to 453 K for 24 h in a sealed NMR tube. After the reaction mixture had been cooled from 453 K to room temperature, single crystals of the title compound, (I), were obtained (yield 20%).

Crystal data

C ₁₈ B ₃ F ₁₅ O ₃	<i>V</i> = 1795.2 (4) Å ³
<i>M_r</i> = 581.61	<i>Z</i> = 4
Monoclinic, <i>C2/c</i>	Mo <i>Kα</i> radiation
<i>a</i> = 16.825 (2) Å	<i>μ</i> = 0.24 mm ⁻¹
<i>b</i> = 13.1810 (13) Å	<i>T</i> = 173 K
<i>c</i> = 8.1049 (12) Å	0.28 × 0.28 × 0.26 mm
<i>β</i> = 92.846 (12)°	

Data collection

Stoe IPDS II two-circle diffractometer	9608 measured reflections
Absorption correction: multi-scan (<i>X-AREA</i> ; Stoe & Cie, 2001)	1680 independent reflections
<i>T_{min}</i> = 0.935, <i>T_{max}</i> = 0.939	1358 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.072

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.037	179 parameters
<i>wR</i> (<i>F</i> ²) = 0.103	Δρ _{max} = 0.29 e Å ⁻³
<i>S</i> = 1.05	Δρ _{min} = -0.21 e Å ⁻³
1680 reflections	

The very strong $\bar{4}02$ reflection is unfortunately missing from the data set because it was not measured.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3434). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Anulewicz-Ostrowska, R., Luliński, S., Serwatowski, S. & Suwińska, K. (2000). *Inorg. Chem.* **39**, 5763–5767.
- Avent, A. G., Lawrence, S. E., Meehan, M. M., Russell, M. M. & Spalding, T. R. (2002). *Collect. Czech. Chem. Commun.* **67**, 1051–1060.
- Beckett, M. A., Strickland, G. C., Varma, K. S., Hibbs, D. E., Hursthouse, M. B. & Malik, K. M. A. (1997). *J. Organomet. Chem.* **535**, 33–41.
- Bhuvanesh, N. S. P., Reibenspies, J. H., Zhang, Y. & Lee, P. L. (2005). *J. Appl. Cryst.* **38**, 632–638.
- Boese, R., Polk, M. & Bläser, D. (1987). *Angew. Chem. Int. Ed.* **26**, 245–247.
- Bolte, M. (2004). Private communication (CCDC 243438). CCDC, Cambridge, England.
- Bolte, M. & Lerner, H.-W. (2011). *J. Chem. Crystallogr.* **41**, 132–136.
- Brock, C. P., Minton, R. P. & Niedenzu, K. (1987). *Acta Cryst.* **C43**, 1775–1779.
- Franz, D., Lerner, H.-W., Seven, Ö. & Bolte, M. (2009). Private communication (CCDC 757641). CCDC, Cambridge, England.
- Haberecht, M. C., Bolte, M., Wagner, M. & Lerner, H.-W. (2005). *J. Chem. Crystallogr.* **35**, 657–665.
- Jones, P. G. & Zerbe, E.-M. (2004). Private communication (CCDC 231365). CCDC, Cambridge, England.
- Lerner, H.-W. (2005). *Coord. Chem. Rev.* **249**, 781–798.
- Meyer-Wegner, F., Nadj, A., Bolte, M., Auner, N., Wagner, M., Holthausen, M. C. & Lerner, H.-W. (2011). *Chem. Eur. J.* **17**, 4715–4719.
- Meyer-Wegner, F., Scholz, S., Sänger, I., Schödel, F., Bolte, M., Wagner, M. & Lerner, H.-W. (2009). *Organometallics*, **28**, 6835–6837.
- Neumüller, B. & Gahlmann, F. (1991). *J. Organomet. Chem.* **414**, 271–283.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (2001). *X-Area*. Stoe & Cie, Darmstadt, Germany.