

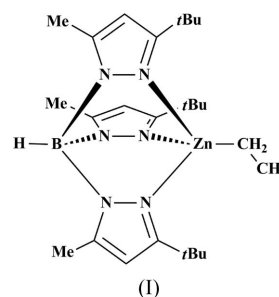
Ethyl[tris(3-*tert*-butyl-5-methylpyrazol-1-yl)hydridoborato]zinc(II)Mukesh Kumar,^a Elizabeth T. Papish^{a*} and Matthias Zeller^{b*}^aDepartment of Chemistry, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, USA, and ^bYoungstown State University, Department of Chemistry, One University Plaza, Youngstown, OH 44555-3663, USA
Correspondence e-mail: ep322@drexel.edu, mzeller@ysu.eduReceived 27 May 2010
Accepted 23 June 2010
Online 7 July 2010

The X-ray crystal structure of the title compound, [Zn(C₂H₅)(C₂₄H₄₀BN₆)] or Tp^{*t*Bu,Me}ZnEt [Tp^{*t*Bu,Me} is tris(3-*tert*-butyl-5-methylpyrazolyl)hydridoborate], reveals a distorted tetrahedral geometry around the Zn atom. The Zn center is coordinated by three N atoms of the borate ligand and by one C atom of the ethyl group. The present structure and other tetrahedral Tp zinc alkyl complexes are compared with similar Ttz ligands (Ttz is 1,2,4-triazolylborate), but no major differences in the structures are noted, and it can be assumed that variation of the substitution pattern of Tp or Ttz ligands has little or no influence on the geometry of alkylzinc complexes. Refinement of the structure is complicated by a combination of metric pseudosymmetry and twinning. The metrics of the structure could also be represented in a double-volume *C*-centered orthorhombic unit cell, and the structure is twinned by one of the orthorhombic symmetry operators not present in the actual structure. The twinning lies on the borderline between pseudomerohedral and nonmerohedral. The data were refined as being nonmerohedrally twinned, pseudomerohedrally twinned and untwinned. None of the approaches yielded results that were unambiguously better than any of the others: the best fit between structural model and data was observed using the nonmerohedral approach which also yielded the best structure quality indicators, but the data set is less than 80% complete due to rejected data. The pseudomerohedral and the untwinned structures are complete, but relatively large residual electron densities that are not close to the metal center are found with values up to three times higher than in the nonmerohedral approach.

Comment

Tris(pyrazolyl)borate (Tp) ligands are known for their applications in modeling of enzymatic active sites (Pettinari, 2008). This is due to the fact that pyrazole rings roughly approximate

the facial coordination of three histidines to a metal and, through the use of a third-position bulky substituent at the pyrazole ring, control of the coordination geometry is possible. We have been interested in the active-site modeling of the enzyme carbonic anhydrase which possesses an *N,N,N,O*-coordination motif. In this regard, we have recently reported the synthesis and structure of Ttz^{*t*Bu,Me}ZnEt [Ttz^{*t*Bu,Me} is tris(3-*tert*-butyl-5-methyl-1,2,4-triazolyl)borate] (Kumar *et al.*, 2010). The steric factors in Tp^{*t*Bu,Me}ZnEt and Ttz^{*t*Bu,Me}ZnEt are similar. However, the third N atom in the triazole ring makes the Ttz ligand a slightly weaker electron donor, as measured by comparison of carbonyl stretching vibrations in copper carbonyl complexes (Papish *et al.*, 2008). These features motivated us to determine the crystal structure of Tp^{*t*Bu,Me}ZnEt, (I), and to make structural comparisons between these two and other related compounds.



Refinement of the structure was complicated by a combination of metric pseudosymmetry and twinning. The structure was found to exhibit metric pseudosymmetry with a double-volume *C*-centered orthorhombic unit cell with the parameters $a = 19.170 \text{ \AA}$, $b = 58.906 \text{ \AA}$ and $c = 9.805 \text{ \AA}$ generated by the transformation matrix $(00\bar{1}/20\bar{1}/010)$. The unit-cell determination indicated that the crystal is twinned by one of the orthorhombic symmetry operations not present in the actual structure, specifically by a 180° rotation around the real *c* axis of the monoclinic cell. The twinning is such that it lies on

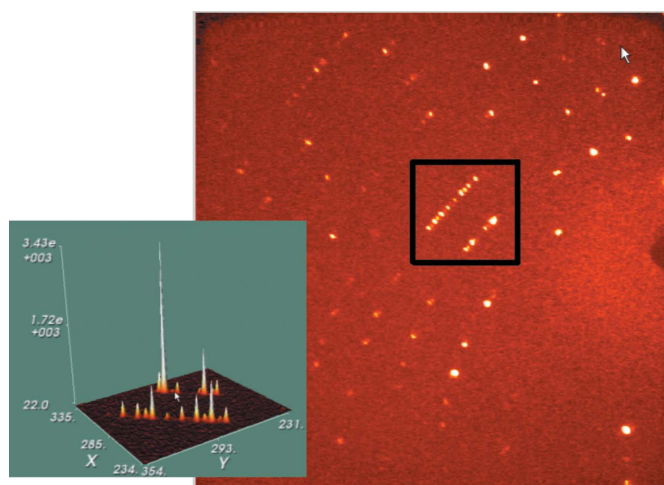


Figure 1

The main picture shows a representative diffraction pattern showing the 'chain of pearl' overlap between the two twin domains. Inset: a three-dimensional intensity view of the section of the frame within the black box in the main picture.

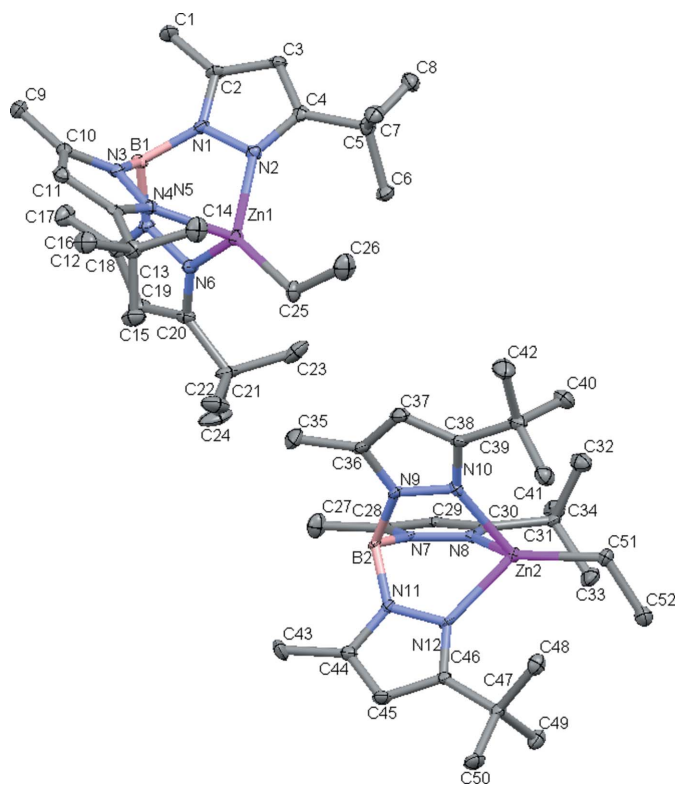


Figure 2
 Perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

the borderline between pseudomerohedral and nonmerohedral. Overlap of neighboring spots was, however, significant with many spots showing multiple consecutive overlaps in a ‘chain of pearls’ fashion (Fig. 1), and many diffraction spots were thus automatically rejected by the integration program (*SAINT*; Bruker, 2009), leading to a data set that is less than 80% complete. In order to overcome these complications, several approaches were tested for the refinement of the structure and the data were handled as being either nonmerohedrally twinned [denoted (*Inm*)], pseudomerohedrally twinned [denoted (*Ipm*)] or untwinned [denoted (*Iunt*)] (see refinement section of this paper for details).

None of the approaches yielded results that were unambiguously better than any of the others: the best fit between structural model and data was observed for the case treated as nonmerohedrally twinned, but the data set is less than 80% complete due to rejected data. All structure quality indicators, however, are best for this approach and residual electron densities are low and located close to the two Zn atoms. In the (*Ipm*) and (*Iunt*) structures relatively large residual electron densities that are not close to the metal center are found with values up to three times higher than in the nonmerohedral approach. Results for all three approaches are given in the *Crystal data*, *Data collection* and *Refinement* tables and the CIF files, and are compared and discussed in more detail in the refinement section of this paper.

All three approaches do, however, yield essentially the same results with no significant changes for any of the critical

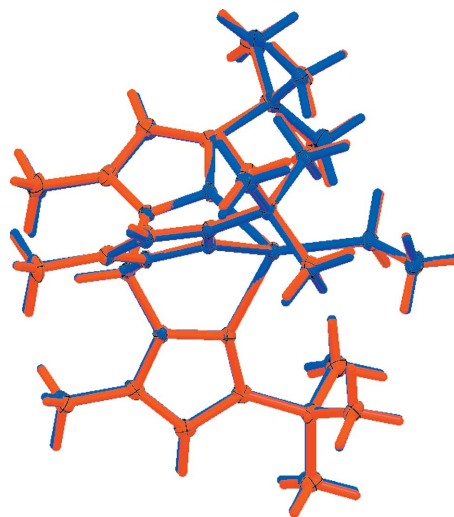


Figure 3
 Least-squares overlay of the two crystallographically independent molecules (shown in red and blue in the electronic version of the paper). The Zn, B and methyl C atom of the ethyl moiety were used to calculate the overlay shown.

parameters such as unit-cell parameters, atom locations, displacement parameters, or bond lengths and angles. Data discussed in the following are based on the structure obtained using the nonmerohedrally twinned approach. The asymmetric unit is comprised of two crystallographically independent molecules which are similar in geometry with virtually identical bond lengths, angles and torsion angles. A displacement ellipsoid plot showing both molecules is given in Fig. 2. Fig. 3 shows a least-squares overlay of the two molecules. The molecules are packed in an alternate fashion in double layers parallel to the *bc* plane of the unit cell, with molecules of one type forming a two-molecule-thick layer parallel to the *bc* plane centered at $x = 0$ that alternates with a double layer of molecules of the other crystallographically independent kind centered at $x = \frac{1}{2}$. The Zn ions are coordinated by three N atoms of the borate ligand and one C atom of the ethyl group. The geometries of the Zn ions in the two molecules (Zn1 and Zn2) are distorted tetrahedral with virtually identical angles around the Zn centers. The N–Zn–C angles are in the ranges 122.0 (1)–128.8 (1) and 121.0 (1)–128.90 (1)°, respectively, for Zn1 and Zn2, while the N–Zn–N angles are in the ranges 88.2 (1)–94.0 (1) and 88.2 (1)–93.9 (1)°, respectively, for Zn1 and Zn2. The respective Zn–C bond distances in both molecules [1.999 (3) and 2.010 (3) Å] and the equivalent Zn–N bonds [2.095 (3)–2.138 (3) Å for Zn1 versus 2.095 (3)–2.129 (3) Å for Zn2] are also very similar in both molecules. No hydrogen bonding or other significant directional interactions are present in the crystal structure.

As described in the introduction, we are interested in the steric and electronic influence that modification of a Tp or Ttz ligand has on the complex geometries and on the resulting complex properties. We have therefore compared the bond distances and angles of the title compound with those of previously known Tp^{R,R'}ZnR'' and Ttz^{R,Me}ZnEt complexes. The Zn–C distances observed in the title compound are slightly longer than those observed in Tp^{(CF₃)₂}ZnEt [Zn–C =

1.959 (6) Å; Diaz *et al.*, 2003], (Tp^{Ph})ZnMe [1.950 (4) Å; Alsfasser *et al.*, 1993], (Tp^{tBu})ZnMe [1.971 (4) Å; Yoon & Parkin, 1991] and Tp^{ind}ZnMe [Tp^{ind} is tris(indazolyl)borate; 1.965 (5) Å; Chisholm *et al.*, 2000]. The distances in the title compound are closer in value to those found in Ph(Tp^{tBu})ZnMe [1.994 (2) Å; Kisko *et al.*, 2000], (Tp^{Me₂})ZnMe [1.981 (8) Å; Looney *et al.*, 1995] and (Ttz^{tBu,Me})ZnEt [1.993 (5) Å] and (Ttz^{Ph,Me})ZnEt [1.983 (2) Å] (Kumar *et al.*, 2010). The average Zn–N bond distances are within their relative standard deviations identical to those in the above Tp^{R,R'}ZnR'' and (Ttz^{R,Me})ZnEt compounds (the average deviation is less than 0.08 Å) and the N–Zn–N and N–Zn–C angles (see above) are also virtually identical (within 3°). On the basis of these data, no major differences in the structures are noted, and it can be assumed that variation of the substitution pattern of Tp or Ttz ligands has little or no influence on the geometry of alkylzinc complexes.

Experimental

A solution of Tl(Tp^{tBu,Me}) (0.210 g, 0.334 mmol; Trofimenko *et al.*, 1992) in CH₂Cl₂ (20 ml) in a flask under an N₂ atmosphere was combined with Et₂Zn (500 µl, 0.500 mmol, 1.0 M in hexane). The reaction mixture turned gray immediately and formation of a black precipitate was observed. After 4 h, the contents were filtered and the volatiles were removed from the filtrate under vacuum. A white solid, *viz.* (Tp^{tBu,Me})ZnEt, was isolated and purified by recrystallization from a mixture of dichloromethane and hexane (1:1 *v/v*). The yield of the product was 0.155 g (90%). Crystals of X-ray diffraction quality were grown by layering hexane on to the dichloromethane solution of the compound in air. ¹H NMR (C₆D₆): δ 1.33 (*q*, 2H, ZnCH₂CH₃, ³J_{H–H} = 8.0 Hz), 1.46 [*s*, 27H, (CH₃)₃C], 2.00 (*t*, 3H, ZnCH₂CH₃, ³J_{H–H} = 8.0 Hz), 2.16 (*s*, 9H, CH₃), 5.70 [*s*, 3H, 4-H(pz)]; ¹³C NMR (C₆D₆): δ 8.06 (ZnCH₂CH₃), 13.18 (CH₃), 14.82 (ZnCH₂CH₃), 31.33 [C(CH₃)₃], 32.20 [C(CH₃)₃], 103.37 (4-pz), 143.65 (5-pz), 163.52 (3-pz); IR (cm⁻¹): 2551.58 (ν_{B–H}); CI–MS: *m/z* = 516.306454 [*M*]⁺ (experimental), 516.309022 [*M*]⁺ (calculated); all peaks showed the expected isotopic pattern.

(Inm), nonmerohedrally twinned data

Crystal data

[Zn(C ₂ H ₅)(C ₂₄ H ₄₀ BN ₆)]	<i>V</i> = 5523 (2) Å ³
<i>M_r</i> = 517.86	<i>Z</i> = 8
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 30.803 (8) Å	<i>μ</i> = 0.91 mm ⁻¹
<i>b</i> = 9.796 (3) Å	<i>T</i> = 100 K
<i>c</i> = 19.157 (5) Å	0.40 × 0.36 × 0.06 mm
<i>β</i> = 107.174 (4)°	

Data collection

Bruker SMART APEX CCD diffractometer	26184 measured reflections
Absorption correction: multi-scan (TWINABS; Bruker, 2008)	11153 independent reflections
<i>T</i> _{min} = 0.591, <i>T</i> _{max} = 0.746	9218 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.034

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.049	640 parameters
<i>wR</i> (<i>F</i> ²) = 0.105	H-atom parameters constrained
<i>S</i> = 1.09	Δ <i>ρ</i> _{max} = 0.71 e Å ⁻³
11153 reflections	Δ <i>ρ</i> _{min} = -0.48 e Å ⁻³

(Ipm), pseudomerohedrally twinned data

Crystal data

[Zn(C ₂ H ₅)(C ₂₄ H ₄₀ BN ₆)]	<i>V</i> = 5535.2 (12) Å ³
<i>M_r</i> = 517.86	<i>Z</i> = 8
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 30.830 (4) Å	<i>μ</i> = 0.91 mm ⁻¹
<i>b</i> = 9.8047 (12) Å	<i>T</i> = 100 K
<i>c</i> = 19.170 (2) Å	0.40 × 0.36 × 0.06 mm
<i>β</i> = 107.2112 (18)°	

Data collection

Bruker SMART APEX CCD diffractometer	37325 measured reflections
Absorption correction: multi-scan (SADABS in APEX2; Bruker, 2009)	13453 independent reflections
<i>T</i> _{min} = 0.606, <i>T</i> _{max} = 0.746	11426 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.038

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.061	640 parameters
<i>wR</i> (<i>F</i> ²) = 0.147	H-atom parameters constrained
<i>S</i> = 1.08	Δ <i>ρ</i> _{max} = 1.69 e Å ⁻³
13453 reflections	Δ <i>ρ</i> _{min} = -0.76 e Å ⁻³

(Iunt), untwinned data

Crystal data

[Zn(C ₂ H ₅)(C ₂₄ H ₄₀ BN ₆)]	<i>V</i> = 5535.2 (12) Å ³
<i>M_r</i> = 517.86	<i>Z</i> = 8
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 30.830 (4) Å	<i>μ</i> = 0.91 mm ⁻¹
<i>b</i> = 9.8047 (12) Å	<i>T</i> = 100 K
<i>c</i> = 19.170 (2) Å	0.40 × 0.36 × 0.06 mm
<i>β</i> = 107.2112 (18)°	

Data collection

Bruker SMART APEX CCD diffractometer	36280 measured reflections
Absorption correction: multi-scan (SADABS in APEX2; Bruker, 2009)	13453 independent reflections
<i>T</i> _{min} = 0.606, <i>T</i> _{max} = 0.746	11426 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.037

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.074	639 parameters
<i>wR</i> (<i>F</i> ²) = 0.186	H-atom parameters constrained
<i>S</i> = 1.25	Δ <i>ρ</i> _{max} = 2.16 e Å ⁻³
13453 reflections	Δ <i>ρ</i> _{min} = -0.89 e Å ⁻³

The structure was found to exhibit metric pseudosymmetry with a double-volume *C*-centered orthorhombic unit cell, with the parameters *a* = 19.170 Å, *b* = 58.906 Å and *c* = 9.805 Å, generated from the true cell by the transformation matrix (001̄/201̄/010). The unit-cell determination indicated that the crystal is twinned by one of the orthorhombic symmetry operations not present in the actual structure in a fashion that is on the borderline between pseudomerohedral and nonmerohedral twinning. Two orientation matrices found using CELL_NOW (Bruker, 2005) are related by a 180° rotation around the real *c* axis. Integration with both moieties gave a transformation matrix of (-0.99861, -0.01191, -0.95577/0.00145, -0.99999, 0.00007/-0.00289, -0.00239, 0.99862). Overlap of neighboring spots was however significant, with many spots showing multiple consecutive overlaps in a 'chain of pearls' fashion (Fig. 1) and which were thus automatically rejected by the integration program as spots that

'exceed the queue size' (*SAINT*; Bruker, 2009). Using the default *SAINT* parameters for treating twin overlaps resulted in 19535 diffraction spots (out of a predicted 56901) being rejected. Of the unrejected data, 1260 (946 unique) involve domain 1 only (mean $I/\sigma = 14.9$), 1227 (936 unique) involve domain 2 only (mean $I/\sigma = 5.2$) and 24922 (13489 unique) involve both domains (mean $I/\sigma = 7.0$). Two data points (both unique) involve three domains (mean $I/\sigma = 32.4$). Of the overlapping spots, 19819 are partial overlaps, 4672 major overlaps and 433 full overlaps. Attempts to collect data at a larger crystal-to-detector distance did not significantly lower the number of rejected reflections. Other crystals from the same batch of material showed the same type of twinning with the same spot overlap problems.

Refinement of the structure with this data set using the HKLF5 routine (Sheldrick, 2008) with the unrejected spots proceeded smoothly with an R_1 value of 0.0486 [$R[F^2 > 2\sigma(F^2)]$] and a twin fraction of 0.1289 (6), but the completeness of the data set out to a resolution of 0.75 Å ($\theta = 28.28^\circ$) does not exceed 80%. The resulting data set is reported as the 'nonmerohedral' structure, *viz.* (*Inm*).

Changing the default twinning parameters used in *SAINT* for the 'Queue Length', the 'Separations Factor' or the 'Maximum Range' did not lead to an improved data set. Variation of the 'Queue Length' did not increase the number of reflections integrated. Increasing the value of the 'Separations Factor' and the 'Maximum Range' did result in fewer reflections being rejected. However, even with modest changes the overall R_1 value increased to unacceptably high values indicating inclusion of many incorrectly integrated diffraction spots: for example, increasing the 'Separations Factor' from 1.0 to 1.1 and the 'Maximum Range' from 1.3 to 1.4 yielded a completeness of 91.5%, but at the cost of an increase in the value of R_1 to 7.7%, a value that is even larger than that obtained when twinning was totally ignored (see below). All other structure quality indicators were worse than when twinning was ignored entirely.

As the twinning in the title compound is at the borderline between pseudomerohedral and nonmerohedral, the data were also integrated using the major domain only and treated as pseudomerohedrally twinned. A twin law (101/0 $\bar{1}$ 0/00 $\bar{1}$) closely similar to the actual transformation matrix was used instead of the HKLF5 two-domain refinement: the R_1 value for this (*Ipm*) structure refined to 6.1%, the twin fraction to 0.0473 (6), with a 98% complete data set up to 28.8° in θ . Complete neglect of all twinning [*i.e.* refinement of the above structure without allowance for pseudomerohedral twinning, the (*Iunt*) structure] results in an R_1 value of 7.4%.

A comparison of the three refinement approaches showed that the best fit between structural model and data was observed for the data treated as nonmerohedrally twinned. R_1 values are lowest and in the range expected based on the data R_{int} and R_σ values. The goodness-of-fit is in the normal range and the twinning ratio is as expected based on the intensities of the two domains. Probably most importantly, the residual electron densities are low and located close to the two Zn centers with values of 0.71 (0.902 Å from Zn1) and 0.54 e Å⁻³ (0.904 Å from Zn1). In the (*Ipm*) and the (*Iunt*) structures, however, relatively large residual electron densities are found remote from the metal centers: the values are 1.69, 1.15 and 1.14 e Å⁻³ for the (*Ipm*) structure, and 2.16 and 1.38 e Å⁻³ for the (*Iunt*) structure. All other

structure quality indicators (R_1 values, goodness-of-fit, *SHELXL* weighting schemes, *etc.*) also indicate that the nonmerohedrally twinned treatment of the data is the most appropriate, even if the data are incomplete.

The structural model used in all refinements is identical. H atoms attached to C atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H distances of 0.98 (CH₃) or 0.95 Å (C–H), B–H distances of 1.00 Å and $U_{iso}(H)$ values of 1.2 $U_{eq}(B/C)$, except that $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

For all determinations, data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003; Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*. Molecular graphics: *Mercury* (CCDC, 2009; Macrae *et al.*, 2008) for (*Inm*). For all compounds, software used to prepare material for publication: *SHELXTL* and *pubCIF* (Westrip, 2010).

The diffractometer was funded by NSF grant No. 0087210, by the Ohio Board of Regents grant No. CAP-491, and by YSU.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3097). Services for accessing these data are described at the back of the journal.

References

- Alsasser, R., Powell, A. K., Trofimenko, S. & Vahrenkamp, H. (1993). *Chem. Ber.* **126**, 685–694.
- Bruker (2003). *SHELXTL*. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2005). *CELL_NOW*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2008). *TWINABS*. Version 2008/2. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2009). *APEX2* [Version 2009.7-0, includes *SAINT* (Version 7.66A) and *SADABS* (Version 2008/1)]. Bruker AXS Inc., Madison, Wisconsin, USA.
- CCDC (2009). *Mercury CSD*. Version 2.3, build RC4. Cambridge Crystallographic Data Centre, Cambridge, England.
- Chisholm, M. H., Eilerts, N. W., Huffman, J. C., Iyer, S. S., Pacold, M. & Phomphrai, K. (2000). *J. Am. Chem. Soc.* **122**, 11845–11854.
- Diaz, H. V. R. & Jin, W. (2003). *Inorg. Chem.* **42**, 5034–5036.
- Kisko, J. L., Fillebeen, T., Hascall, T. & Parkin, G. (2000). *J. Organomet. Chem.* **596**, 22–26.
- Kumar, M., Papish, E. T., Zeller, M. & Hunter, A. (2010). *Dalton Trans.* pp. 59–61.
- Looney, A., Han, R., Gorrell, I. B., Cornebise, M., Yoon, K., Parkin, G. & Rheingold, A. L. (1995). *Organometallics*, **14**, 274–288.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Papish, E. T., Donahue, T. M., Wells, K. R. & Yap, G. P. A. (2008). *Dalton Trans.* pp. 2923–2925.
- Pettinari, C. (2008). *Scorpionates II: Chelating Borate Ligands*. Singapore: World Scientific Publishing Co.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Trofimenko, S., Calabrese, J. C., Kochi, J. K., Wolowiec, S. S., Hulsbergen, F. B. & Reedijk, J. (1992). *Inorg. Chem.* **31**, 3943–3950.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.
- Yoon, K. & Parkin, G. (1991). *J. Am. Chem. Soc.* **113**, 8414–8418.