

# [Bis(3,5-diisopropylpyrazol-1-yl- $\kappa$ N<sup>2</sup>)-dihydroborato](triphenylphosphane- $\kappa$ P)copper(I)

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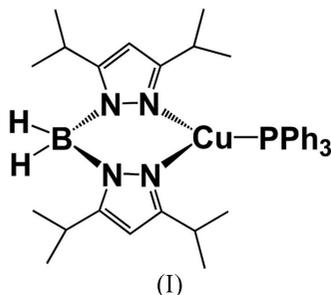
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In the title compound, [Cu(C<sub>18</sub>H<sub>32</sub>BN<sub>4</sub>)(C<sub>18</sub>H<sub>15</sub>P)], the Cu<sup>I</sup> ion is coordinated by two N atoms from the anionic bidentate chelating bis(3,5-diisopropylpyrazol-1-yl)dihydroborate ligand [average Cu–N distance = 1.994 (3) Å] and the P atom from a triphenylphosphane ligand [Cu–P distance = 2.1676 (8) Å] in a trigonal geometry [the sum of the angles around the Cu<sup>I</sup> atom is 359.6 (1)°]. The N–Cu–N angle between adjacent coordinated pyrazole-ring N atoms is 98.99 (9)°, while the average N–Cu–P angle between the coordinated pyrazole N atom and the triphenylphosphane P atom is 130.3 (1)°.

**Keywords:** crystal structure; scorpionates; copper compound; phosphane ligand.

## 1. Introduction

The late Professor Swiatoslaw Trofimenko first reported the tris(pyrazolyl)borate (Tpb) ligand system (Trofimenko, 1966). Ever since then, these anionic ligands have been used in inorganic, bioinorganic, and organometallic chemistry owing to the fact that they can bind metals in versatile coordination



modes and are useful for the preparation of complexes of elements throughout the periodic table (Trofimenko, 1972,

1993, 2004). By introducing bulkier substituents in the 3-position of the pyrazole rings, the formation of unreactive and coordinatively saturated complexes of type [M{HB(3-Rpz)<sub>3</sub>}<sub>2</sub>] (M = Tl<sup>I</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>; R = Ph, *t*-Bu) could easily be avoided (Calabrese *et al.*, 1986; Trofimenko *et al.*, 1987). Thereafter, many combinations of aliphatic and aromatic substituents were introduced in the pyrazole 3-, 4-, and 5-positions to explore novel coordination chemistry (Trofimenko, 1999; Pettinari, 2008).

## 2. Experimental

### 2.1. Synthesis and crystallization

For the preparation of K[H<sub>2</sub>B{3,5-(*i*-Pr)<sub>2</sub>pz}<sub>2</sub>], 3,5-diisopropylpyrazole (4.00 g, 26.3 mmol) (Kitajima, Fujisawa, Fujimoto *et al.*, 1992) was added at room temperature to KBH<sub>4</sub> (0.709 g, 13.1 mmol) suspended in bis(2-methoxyethyl) ether (14 ml). The reaction mixture was heated at *ca* 408–413 K while being stirred for 20 h. The solvent was then removed under reduced pressure and the product was extracted with dichloromethane and filtered to remove any insoluble material. The dichloromethane solvent was then removed under reduced pressure to give the ligand as a white solid. The product was purified by sublimation (yield 65%). Analysis calculated: C 61.01, H 9.10, N 15.81%; found: C 60.72, H 9.10, N 15.81%. IR (KBr disc,  $\nu$ , cm<sup>-1</sup>): 2962 (*s*), 2472 (*m*), 2407 (*m*), 2378 (*m*), 2290 (*m*).

For the preparation of [Cu{H<sub>2</sub>B{3,5-(*i*-Pr)<sub>2</sub>pz}<sub>2</sub>}(PPh<sub>3</sub>)], *viz.* (I), K[H<sub>2</sub>B{3,5-(*i*-Pr)<sub>2</sub>pz}<sub>2</sub>] (100 mg, 0.28 mmol) in dichloromethane (10 ml) was added to CuCl (33.5 mg, 0.34 mmol) in acetonitrile (10 ml), and then stirred for 30 min at room temperature in an inert atmosphere glove-box. Triphenylphosphane (81.4 mg, 0.31 mmol) in dichloromethane (5 ml) was added and the resulting mixture was stirred overnight. The solvents were removed under reduced pressure. The resulting colourless solid was extracted into dichloromethane, and filtered over Celite. The filtrate was concentrated and cooled to 243 K to obtain colourless crystals (yield 52.1 mg, 29%) of (I). HRMS–ESI (*m/z*): [M + H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>48</sub>BCuN<sub>4</sub>P: 641.301; found: 641.366. IR (KBr disc,  $\nu$ , cm<sup>-1</sup>): 2959 (*s*), 2467 (*m*), 2353 (*m*), 2324 (*m*), 2281 (*m*), 1164 (*s*), 694 (*s*). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  0.88 [*d*, *J* = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.22 [*d*, *J* = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>], 2.58 [*sept*, *J* = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>], 3.41 [*sept*, *J* = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>], 5.72 [*s*, 2H, 4-*H*(pz)], 7.33–7.56 (*m*, 15H, PPh<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 242 MHz):  $\delta$  8.54 (*br s*, PPh<sub>3</sub>).

### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For the structure refinement of X-ray diffraction data, H atoms were placed in calculated positions, treated as riding, and constrained with *U*<sub>iso</sub>(H) = 1.2 or 1.5 times *U*<sub>eq</sub>(parent). The absolute structure was deduced based on the Flack parameter, 0.004 (10), and refined using 1237 Friedel pairs (Flack, 1983).

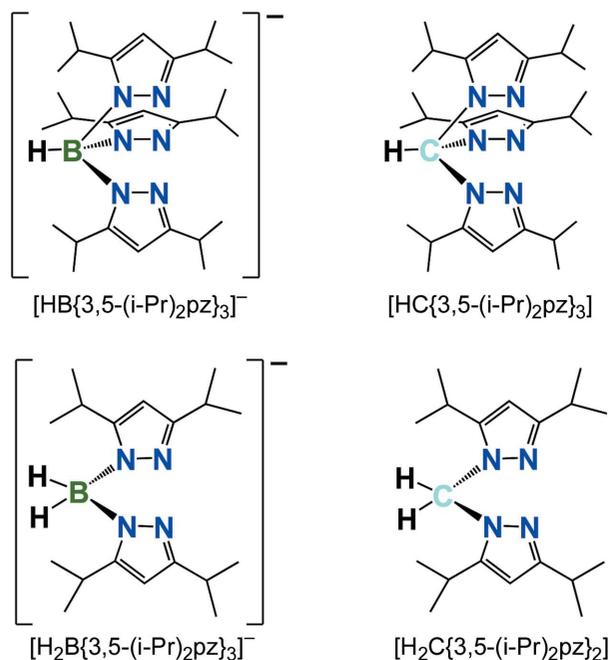
**Table 1**  
Experimental details.

Crystal data	
Chemical formula	[Cu(C <sub>18</sub> H <sub>32</sub> BN <sub>4</sub> )(C <sub>18</sub> H <sub>15</sub> P)]
<i>M<sub>r</sub></i>	641.12
Crystal system, space group	Monoclinic, <i>Cc</i>
Temperature (K)	184
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.3372 (5), 14.3257 (5), 18.4712 (10)
$\beta$ (°)	97.6540 (8)
<i>V</i> (Å <sup>3</sup> )	3497.8 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.70
Crystal size (mm)	0.40 × 0.20 × 0.20
Data collection	
Diffractometer	Rigaku Mercury70 diffractometer
Absorption correction	Multi-scan ( <i>REQAB</i> ; Rigaku, 1998)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.736, 0.869
No. of measured, independent and observed [ <i>F</i> <sup>2</sup> > 2.0 $\sigma$ ( <i>F</i> <sup>2</sup> )] reflections	14044, 5245, 5155
<i>R<sub>int</sub></i>	0.020
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.649
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.030, 0.081, 1.06
No. of reflections	5245
No. of parameters	388
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.37, -0.25
Absolute structure	Flack (1983), 1237 Friedel pairs
Flack parameter	0.004 (10)

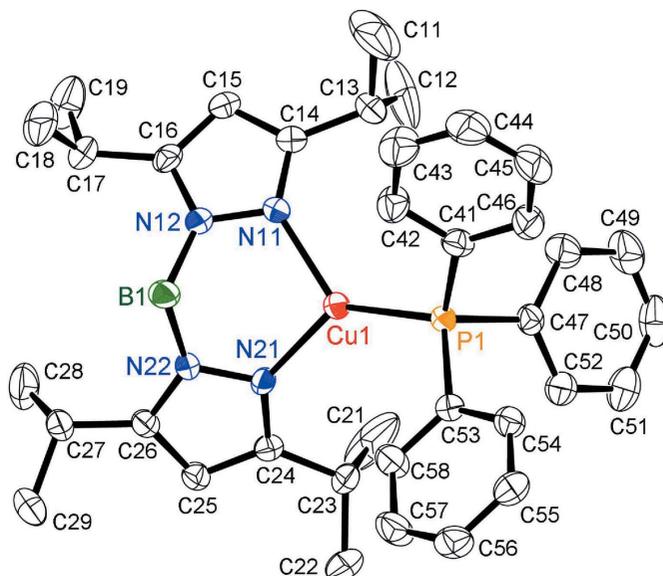
Computer programs: *CrystalClear* (Rigaku, 2010), *CrystalStructure* (Rigaku, 2010), *SIR97* (Altomare *et al.*, 1999), *SHELXL97* (Sheldrick, 2008) and *CrystalStructure* (Rigaku, 2010).

### 3. Results and discussion

We applied this methodology by using the anionic ligand tris(3,5-diisopropylpyrazol-1-yl)hydroborate(1-), denoted [HB-



**Figure 1**  
Schematic drawing of the scorpionate derivatives.



**Figure 2**  
The molecular structure of [Cu{H<sub>2</sub>B[3,5-(*i*-Pr)<sub>2</sub>pz]<sub>2</sub>}(PPh<sub>3</sub>)] (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

{3,5-(*i*-Pr)<sub>2</sub>pz}<sub>3</sub>}<sup>-</sup>, to prepare peroxidocopper(II) complexes (Kitajima, Fujisawa, Fujimoto *et al.*, 1992; Baldwin *et al.*, 1992) and thiolatocopper(II) complexes (Kitajima, Fujisawa, Tanaka & Morooka, 1992; Randall *et al.*, 2000) as models for oxy-hemocyanin and blue copper proteins, respectively (Fig. 1). Therefore, the [HB{3,5-(*i*-Pr)<sub>2</sub>pz}<sub>3</sub>}<sup>-</sup> ligand has played an important role in developing copper-containing protein model complexes in the field of bioinorganic chemistry. Expanding this ligand system, we introduced *tert*-butyl groups in the 3-positions of the pyrazole rings, leading to the ligand [tris(3-*tert*-butyl-5-isopropylpyrazol-1-yl)hydroborate(1-)], [HB-(3-*t*-Bu-5-*i*-Prpz)<sub>3</sub>}<sup>-</sup>. This ligand was used to prepare mononuclear complexes selectively. We also reported the structural influences of *tert*-butyl groups on copper(II) complexes (Fujisawa *et al.*, 1994, 2000).

In addition, we prepared analogous tris(pyrazolyl)methane (Tpm) as another neutral tripodal N<sub>3</sub> ligand. The Tpm ligand contains a C atom in place of the B atom of Tpb ligands, and is therefore a neutral analogue of the Tpb ligand system. Exploiting the charge difference of these ligands enabled the isolation of the copper(I) carbonyl complexes with high CO stretching frequencies: for example,  $\nu$ (C–O) is 2056 cm<sup>-1</sup> for [Cu{HB[3,5-(*i*-Pr)<sub>2</sub>pz]<sub>3</sub>}(CO)] and 2107 cm<sup>-1</sup> for the analogous complex [Cu{HC[3,5-(*i*-Pr)<sub>2</sub>pz]<sub>3</sub>}(CO)]PF<sub>6</sub> (Fujisawa *et al.*, 2004, 2006).

The results summarized above provide key insight into second coordination sphere effects caused by the different ligands employed – that is, the influence of the total charge, the steric hindrance, and the electronic effects of the ligand on the structures, properties, and reactivity of the resulting complexes. These findings prompted us to attempt a comparison of the structures, spectroscopic properties, and reactivities of the corresponding copper(I) complexes with compounds containing the analogous neutral bidentate ligand bis(3,5-di-

**Table 2**

Selected geometric parameters (Å, °).

Cu1—P1	2.1676 (8)	Cu1—N11	1.990 (3)
Cu1—N21	1.997 (2)	Cu1···B1	3.033 (4)
P1—Cu1—N11	127.93 (6)	P1—Cu1—N21	132.71 (7)
N11—Cu1—N21	98.99 (9)	N12—B1—N22	109.1 (3)

isopropylpyrazol-1-yl)methane,  $[\text{H}_2\text{C}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_2]$  (Fujisawa *et al.*, 2007). In addition, we also studied complexes with the anionic bidentate ligand bis(3,5-diisopropylpyrazol-1-yl)-dihydroborate(1-),  $[\text{H}_2\text{B}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_2]^-$ . The synthetic methods used to prepare bis(pyrazolyl)borate derivatives, such as  $[\text{H}_2\text{B}\{3,5\text{-Me}_2\text{pz}\}_2]^-$  (Trofimenko, 1967),  $[\text{H}_2\text{B}\{3\text{-}t\text{-Bupz}\}_2]^-$  (Trofimenko *et al.*, 1987), and  $[\text{H}_2\text{B}\{3,5\text{-}(\text{CF}_3)_2\text{pz}\}_2]^-$  (Dias & Gorden, 1996), have been published previously. In these cases, higher boiling-point solvents, *viz.* *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and toluene, respectively, were used for the ligand syntheses. Finally, we succeeded in the preparation of the desired  $[\text{H}_2\text{B}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_2]^-$  ligand using bis(2-methoxyethyl) ether (diglyme) as solvent.

Copper(I) complexes ligated by this bidentate ligand are very unstable towards dioxygen. Therefore, we prepared and crystallized the corresponding, more stable, triphenylphosphane copper(I) complex,  $[\text{Cu}\{\text{H}_2\text{B}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_2\}(\text{PPh}_3)]$ , (I), instead. The title complex crystallizes in the monoclinic space group *Cc*. As shown in Fig. 2, the  $\text{Cu}^{\text{I}}$  ion adopts a trigonal-planar geometry [the sum of the angles around the  $\text{Cu}^{\text{I}}$  center is  $359.6(1)^\circ$ ; Table 2]. The  $\text{Cu}^{\text{I}}$  center deviates slightly [0.0708 (7) Å] from the N(pz)—N(pz)—P(PPh<sub>3</sub>) plane. The N—Cu—N angle between adjacent coordinated pyrazole-ring N atoms is  $98.99(9)^\circ$ , while the average N—

**Table 3**

Cu—P bond lengths (Å) in triphenylphosphane copper(I) complexes.

Complex	Cu—P	Reference
$[\text{Cu}\{\text{H}_2\text{B}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_2\}(\text{PPh}_3)]$	2.1676 (8)	This work
$[\text{Cu}\{\text{H}_2\text{B}\{3,5\text{-}(\text{CF}_3)_2\text{pz}\}_2\}(\text{PPh}_3)]$	2.1753 (8)	Dias <i>et al.</i> (2005)
$[\text{Cu}\{\text{H}_2\text{C}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_2\}(\text{PPh}_3)]\text{ClO}_4$	2.174 (2)	Fujisawa <i>et al.</i> (2007)
$[\text{Cu}\{\text{H}_2\text{C}\{3,5\text{-Me}_2\text{pz}\}_2\}(\text{PPh}_3)]\text{ClO}_4$	2.171 (2)	Chou <i>et al.</i> (2005)
$[\text{Cu}\{\text{HC}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_3\}(\text{PPh}_3)]\text{ClO}_4$	2.159 (4)	Fujisawa <i>et al.</i> (2007)
$[\text{Cu}\{\text{HB}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_3\}(\text{PPh}_3)]$	2.1635 (10)	Fujisawa <i>et al.</i> (2009)
$[\text{Cu}\{\text{HB}\{3\text{-CF}_3\text{-5-Mepz}\}_3\}(\text{PPh}_3)]$	2.2150 (7)	Fujisawa <i>et al.</i> (2009)

Cu—P angle between the coordinated pyrazole N atoms and the triphenylphosphane P atom is  $130.3(1)^\circ$ . With this complex in hand, we now have four different types of scorpionate ligands with identical pyrazolyl substituents (Fig. 3). Hence, we can now compare the effects of the number of N atoms and the charge of the scorpionate, using both anionic poly(pyrazol-1-yl)hydroborates and neutral poly(pyrazol-1-yl)methanes, on the Cu—P bond.

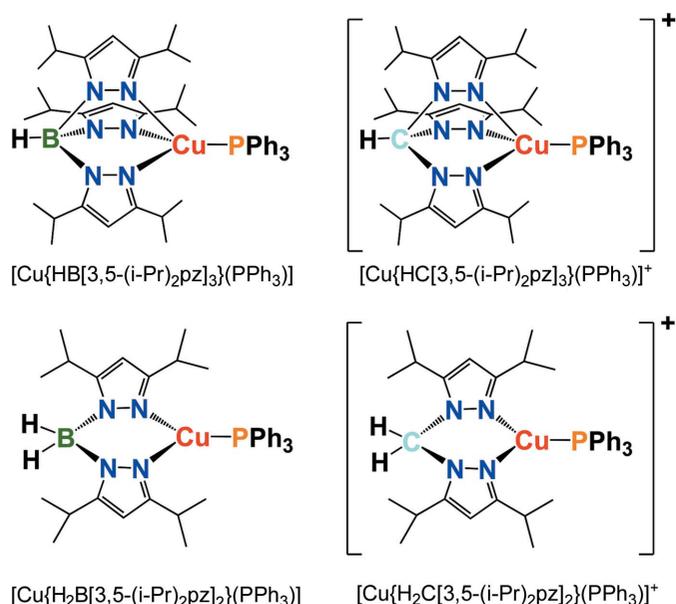
The Cu—P bond distance for (I) is compared with the distances for similar complexes in Table 3. The order of Cu—P bond distances with the same pyrazolyl derivative with isopropyl substituents, arranged by scorpionate, is:  $\text{H}_2\text{C}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_2 > \text{H}_2\text{B}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_2 > \text{HB}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_3 > \text{HC}\{3,5\text{-}(i\text{-Pr})_2\text{pz}\}_3$ . Our studies strongly suggest that the number of N atoms and the charge of the scorpionate control the Cu—P bond strength.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: YP3032). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Baldwin, M. J., Root, D. E., Pate, J. E., Fujisawa, K., Kitajima, N. & Solomon, E. I. (1992). *J. Am. Chem. Soc.* **114**, 10421–10431.
- Calabrese, J. C., Trofimenko, S. & Thompson, J. S. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1122–1123.
- Chou, C. C., Su, C. C. & Yeh, A. (2005). *Inorg. Chem.* **44**, 6122–6128.
- Dias, H. V. & Gorden, J. D. (1996). *Inorg. Chem.* **35**, 318–324.
- Dias, H. R., Richey, S. A., Diyabalanage, H. V. & Thankamani, J. (2005). *J. Organomet. Chem.* **690**, 1913–1922.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Fujisawa, K., Kobayashi, T., Fujita, K., Kitajima, N., Moro-oka, Y., Miyashita, Y., Yamada, Y. & Okamoto, K. (2000). *Bull. Chem. Soc. Jpn.* **73**, 1797–1804.
- Fujisawa, K., Noguchi, Y., Miyashita, Y., Okamoto, K. & Lehnert, N. (2007). *Inorg. Chem.* **46**, 10607–10623.
- Fujisawa, K., Ono, T., Aoki, H., Ishikawa, Y., Miyashita, Y., Okamoto, K., Nakazawa, H. & Higashimura, H. (2004). *Inorg. Chem. Commun.* **7**, 330–332.
- Fujisawa, K., Ono, T., Ishikawa, Y., Amir, N., Miyashita, Y., Okamoto, K. & Lehnert, N. (2006). *Inorg. Chem.* **45**, 1698–1713.
- Fujisawa, K., Tanaka, M., Moro-oka, Y. & Kitajima, N. (1994). *J. Am. Chem. Soc.* **116**, 12079–12080.

**Figure 3**

Schematic drawings of the triphenylphosphane copper(I) complexes discussed in this paper.

- Fujisawa, K., Yoshida, M., Miyashita, Y. & Okamoto, K. (2009). *Polyhedron*, **28**, 1447–1454.
- Kitajima, N., Fujisawa, K., Fujimoto, C., Morooka, Y., Hashimoto, S., Kitagawa, T., Toriumi, K., Tatsumi, K. & Nakamura, A. (1992). *J. Am. Chem. Soc.* **114**, 1277–1291.
- Kitajima, N., Fujisawa, K., Tanaka, M. & Morooka, Y. (1992). *J. Am. Chem. Soc.* **114**, 9232–9233.
- Pettinari, C. (2008). *Scorpionates II: Chelating Borate Ligands*. Singapore: World Scientific Publishing Co.
- Randall, D. W., George, S. D., Hedman, B., Hodgson, K. O., Fujisawa, K. & Solomon, E. I. (2000). *J. Am. Chem. Soc.* **122**, 11620–11631.
- Rigaku (1998). *REQAB*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2010). *CrystalClear and CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Trofimenko, S. (1966). *J. Am. Chem. Soc.* **88**, 1842–1844.
- Trofimenko, S. (1967). *J. Am. Chem. Soc.* **89**, 6288–6294.
- Trofimenko, S. (1972). *Chem. Rev.* **72**, 497–509.
- Trofimenko, S. (1993). *Chem. Rev.* **93**, 943–980.
- Trofimenko, S. (1999). In *Scorpionates: the Coordination Chemistry of Polypyrazolylborate Ligands*. London: Imperial College Press.
- Trofimenko, S. (2004). *Polyhedron*, **23**, 197–203.
- Trofimenko, S., Calabrese, J. C. & Thompson, J. S. (1987). *Inorg. Chem.* **26**, 1507–1514.