involving H atoms are two connecting Br(1) to N(1) and N(2) respectively. A selection of angles between least-squares planes and main torsion angles has been deposited.

References

ALCALÁ-ARANDA, R., FERNÁNDEZ, J., GÓMEZ-BELTRÁN, F. & LARENA, A. (1977). *Cryst. Struct. Commun.* **6**, 635–638.

GARCÍA-GRANDA, S. & GÓMEZ-BELTRÁN, F. (1984*a*). *Acta Cryst.* C**40**, 949–951.

GARCÍA-GRANDA, S. & GÓMEZ-BELTRÁN, F. (1984*b*). *Acta Cryst.* C**40**, 1145–1147.

GARCÍA-GRANDA, S. & GÓMEZ-BELTRÁN, F. (1984*c*). *Acta Cryst.* C**40**, 2037–2038.

GARCÍA-GRANDA, S. & GÓMEZ-BELTRÁN, F. (1986). *Acta Cryst.* C**43**, 236–238.

GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). *SHELXS86*. In *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford: Clarendon Press.

TOFTLUND, H. & SIMONSEN, O. (1984). *Inorg. Chem.* **23**, 4261–4265.

VALERO-CAPILLA, A., ALCALÁ-ARANDA, R. & GÓMEZ-BELTRÁN, F. (1980). *Cryst. Struct. Commun.* **9**, 147–150.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1990). C**46**, 995–998

Structure of 3-(η^6-Hexamethylbenzene)-1,2-dicarba-3-ruthena-*closo*-dodecaborane(11)

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Abstract. $C_{14}H_{29}B_9Ru$, $M_r = 395{\cdot}75$, orthorhombic, $Cmc2_1$, $a = 12{\cdot}994\,(2)$, $b = 10{\cdot}365\,(2)$, $c = 13{\cdot}872\,(2)$ Å, $V = 1868{\cdot}2\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 7·40 cm^{-1}, $F(000) = 808$, room temperature, $R = 0{\cdot}0177$, 890 unique reflections with $F > 3{\cdot}0\sigma(F)$. The structure is based on a 12-vertex RuC_2B_9 icosahedron with the Ru and two C atoms occupying a common deltahedral face. The cluster displays true *closo* geometry and no significant slippage is evident.

Introduction. We have determined the crystal and molecular structure of the closed 12-vertex metalladicarbaborane [3-(η^6-C_6Me_6)-*closo*-3,1,2-$RuC_2B_9H_{11}$] as part of a series to compare and examine for systematic changes in the {Ru(η^6-C_6Me_6)} moiety in a number of polyhedral boron-containing compounds as the nature of the boron-containing fragment varies. The previously reported polyhedral boron-containing structures involving the Ru(η^6-C_6Me_6) centre are those compounds summarized in Table 3. The crystallographically determined molecular structure of the closely related compound [3-(η^6-C_6H_6)-3,1,2-$RuC_2B_9H_{11}$] has previously been reported (Garcia, Green, Stone, Sommerville, Welch, Briant, Cox & Mingos, 1985), but more data are available for comparing the Ru(η^6-C_6Me_6) centres among polyhedral metallaborane structures.

Experimental. A sample of [3-(η^6-C_6Me_6)-3,1,2-$RuC_2B_9H_{11}$] was prepared from [(η^6-C_6Me_6)$RuCl_2$]$_2$,

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

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

	x	y	z	U_{eq}
Ru(3)	5000*	3400·7 (2)	1000†	23·1 (1)
C(11)	4437 (3)	3462 (2)	2527 (3)	34 (1)
C(12)	3881 (3)	2488 (3)	3110 (3)	50 (1)
C(21)	3910 (2)	4399 (3)	1983 (2)	33 (1)
C(22)	2743 (3)	4420 (4)	1980 (3)	56 (1)
C(31)	5552 (2)	5338 (3)	1428 (2)	37 (1)
C(32)	6116 (3)	6334 (4)	847 (3)	56 (1)
C(1)	4362 (3)	1574 (2)	513 (3)	37 (1)
B(4)	3901 (3)	2849 (3)	− 146 (2)	36 (1)
B(5)	3903 (3)	1258 (4)	− 628 (3)	41 (1)
B(6)	5000*	449 (4)	− 187 (4)	46 (1)
B(8)	5000*	3682 (5)	− 595 (3)	33 (1)
B(9)	4317 (3)	2555 (3)	− 1331 (2)	37 (1)
B(10)	5000*	1089 (5)	− 1360 (3)	41 (1)

* Coordinate fixed on special position.
† Coordinate fixed to define origin.

Table 2. *Selected interatomic distances* (Å) *for* [3-(η^6-C_6Me_6)-*closo*-3,1,2-$RuC_2B_9H_{11}$] *with e.s.d.'s in parentheses*

Ru(3)—C(1)	2·175 (5)	Ru(3)—C(11)	2·242 (5)
Ru(3)—B(4)	2·212 (5)	Ru(3)—C(21)	2·222 (5)
Ru(3)—B(8)	2·231 (6)	Ru(3)—C(31)	2·213 (5)
C(1)—C(2^i)	1·657 (10)	B(4)—B(5)	1·780 (7)
C(1)—B(4)	1·715 (6)	B(4)—B(8)	1·781 (6)
C(1)—B(5)	1·723 (7)	B(4)—B(9)	1·757 (7)
C(1)—B(6)	1·729 (7)	B(8)—B(9)	1·788 (7)
B(6)—B(5)	1·763 (7)	B(5)—B(10)	1·759 (7)
B(5)—B(9)	1·756 (7)	B(6)—B(10)	1·757 (9)
B(9)—B(12^i)	1·776 (9)	B(9)—B(10)	1·760 (7)
C(1)—H(1)	1·093 (14)	B(5)—H(5)	1·151 (13)
B(4)—H(4)	1·048 (14)	B(6)—H(6)	1·078 (13)
B(8)—H(8)	1·049 (13)	B(9)—H(9)	0·973 (14)
		B(10)—H(10)	1·131 (14)
C—C(aromatic)		1·408 (5)–1·463 (8)	
C(aromatic)—C(methyl)		1·482 (5)–1·517 (6)	

Symmetry code: (i) $1{\cdot}0 - x, y, z$.

nido-$C_2B_9H_{12}^-$, and tetramethylnaphthalenediamine as described elsewhere (Bown, Plešek, Baše, Štíbr, Fontaine, Greenwood & Kennedy, 1989). A crystal of suitable size (*ca* 0·3 × 0·4 × 0·8 mm) was obtained by the diffusion of pentane into a dichloromethane solution of the title complex. All measurements were made on a Nicolet *P*3/*F* diffractometer; 25 reflections centred ($35{\cdot}0 < 2\theta < 40{\cdot}0°$), graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, ω-scan widths 2° + α-doublet splitting, scan speeds 2·0–29·3° min^{-1} subject to a fast pre-scan. Complete data set (h, $0\rightarrow15$; k, $0\rightarrow12$; l, $0\rightarrow16$; $2\theta_{max} = 50°$) measured over 16 exposure hours with no significant decay of a standard reflection (measured every 50 reflections); 977 unique data, 890 with $F > 3{\cdot}0\sigma(F)$ considered observed and used in structure solution and refinement. Systematic absences (hkl, $h + k = 2n + 1$; $0kl$, k, $l = 2n + 1$) revealed a C-centred cell with three possible space groups *viz* *Ccmm*, *Cc*2*m* or *Ccm*2$_1$, the non-standard settings for *Cmcm*, *Ama*2 and *Cmc*2$_1$ respectively. The cell was transformed appropriately to give the standard setting for each space group in turn, the Patterson map calculated and structure solution then attempted. Only for *Cmc*2$_1$ was a solution obtained and then only after overcoming considerable problems with pseudosymmetry by judiciously selecting peaks from successive Fourier difference syntheses. When all the non-H atoms had been located in this fashion the structure was refined with isotropic thermal parameters using full-matrix least squares. Once convergence had been achieved an empirical absorption correction was applied (Walker & Stuart, 1983) and all atoms then refined with anisotropic thermal parameters. All H atoms were located in a subsequent Fourier difference synthesis. The carbaborane H atoms were freely refined with isotropic thermal parameters, but due to the limited amount of data the methyl H atoms were included in the refinement with an overall isotropic thermal parameter although their positional parameters were not refined (total number of parameters = 140). Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Refinement converged to $R = 0{\cdot}0177$, $wR = 0{\cdot}0187$, $w^{-1} = \sigma^2(F_o) + 0{\cdot}0002(F_o)^2$, $S = 1{\cdot}031$, $\sum w(\Delta F)^2$ minimized, difference synthesis showed max. density of $0{\cdot}20\ \text{e Å}^{-3}$ (min. $-0{\cdot}38\ \text{e Å}^{-3}$); max. $\Delta/\sigma = 0{\cdot}98$ in z of H(1). It should be noted that although this particular space group possesses a polar axis its direction was not determinable because refinement of the enantiomorphous structure produced no significant changes in the refinement parameters or the residuals. All calculations performed on an Amdahl 5850 computer.

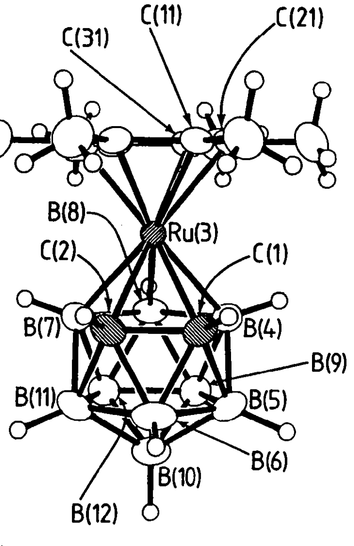

Fig. 1. *ORTEP* drawing of the molecular structure of [3-(η^6-C_6Me_6)-*closo*-3,1,2-$RuC_2B_9H_{11}$], showing numbering system used.

Table 3. *Comparison of ruthenium—carbon distances in the* $\{(\eta^6\text{-}C_6Me_6)Ru\}$ *units of structurally characterized ruthenaboranes and carboranes*

No.	Compound	Type of cluster	Range (Å)	Weighted mean value (Å)	Reference
1	$[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{closo}\text{-}2,1,6\text{-}RuC_2B_7H_9]$	*closo* 10-vertex	2·200 (4)–2·215 (4)	2·208 (6)	*a*
2	$[7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}7\text{-}RuB_{10}H_{13}]^-$	*nido* 11-vertex	2·189 (6)–2·236 (6)	2·211 (17)	*b*
3	$[3\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{closo}\text{-}3,1,2\text{-}RuC_2B_9H_{11}]$	*closo* 12-vertex	2·213 (5)–2·242 (5)	2·226 (12)	*c*
4	$[6\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}6\text{-}RuB_9H_{13}]$	*nido* 10-vertex	2·208 (4)–2·253 (4)	2·231 (18)	*d*
5	$[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}2\text{-}RuB_5H_9]$	*nido* 6-vertex	2·224 (6)–2·250 (5)	2·236 (10)	*d*
6	$[6\text{-}(OMe)\text{-}5\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}5\text{-}RuB_9H_{12}]$	*nido* 10-vertex	2·244 (5)–2·301 (5)	2·266 (17)	*e*
7	$[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}2\text{-}RuB_9H_{13}]$	*nido* 10-vertex	2·266 (6)–2·294 (6)	2·278 (10)	*f*
8	$[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{arachno}\text{-}1\text{-}RuB_8H_{14}]$	*arachno* 9-vertex	2·266 (5)–2·306 (5)	2·284 (15)	*g*
9	$[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}`\textit{nido}'\text{-}1\text{-}RuB_9H_{13}]$	*'isoarachno'* 10-vertex	2·287 (4)–2·307 (4)	2·297 (8)	*f*

References: (*a*) Bown, Jelínek, Štíbr, Heřmánek, Fontaine, Greenwood, Kennedy & Thornton-Pett (1988). (*b*) Bown, Fontaine, Greenwood, Kennedy, & Thornton-Pett (1987*b*). (*c*) This work. (*d*) Bown & Thornton-Pett (1986). (*e*) Bown, Fontaine, Greenwood, Kennedy & Thornton-Pett (1987*a*). (*f*) Bown, Fontaine, Greenwood, Kennedy & MacKinnon (1987). (*g*) Bown, Fontaine, Greenwood, Kennedy & Thornton-Pett (1986).

Programs *SHELX76* (Sheldrick, 1976) and *ORTEP*II (Johnson, 1976).

Discussion. Final fractional coordinates and equivalent isotropic thermal parameters are listed in Table 1,* and the molecular structure and its numbering scheme are shown in Fig. 1. Selected interatomic distances are in Table 2. The closed 12-vertex icosahedral $\{RuC_2B_9\}$ cluster structure [which has a crystallographic mirror plane passing through atoms Ru(3), B(6), B(8) and B(10)] is readily apparent, as is the positioning of the ruthenium and two C atoms in the mutually adjacent 3,1,2 positions. The cluster has true *closo* geometry with no marked slippage or anomalous open-face behaviour as is sometimes observed in areneruthenium polyhedral boron-containing species (Bown, Fontaine, Greenwood, Kennedy & MacKinnon, 1987; Bown, Fontaine, Greenwood, Kennedy, MacKinnon & Thornton-Pett, 1987; Baše, Bown, Štíbr, Fontaine, Greenwood, Kennedy & Thornton-Pett, 1988). Thus the ruthenium-to-carbon cluster distance is somewhat shorter than those to boron, as expected, although there is a marginal tilt of 3·2 (1)° *versus* the mean C(1)C(2)B(7)B(8)B(4) plane of the η^6-arene plane away from the cluster C-atom positions, which may reflect a *trans* influence arising from stronger bonding to B(4)B(8)B(7) *versus* C(1)C(2). The C_6Me_6 ligand is essentially flat with the three independent methyl atoms C(12), C(22) and C(32) lying 0·012 (4), 0·015 (4) and 0·002 (4) Å respectively from the least-squares plane passing through the C_6 ring on the side. The η^6-arene and η^5-C_2B_3 rings each approximate closely to planar, with the Ru(3) atom lying 1·708 (1) Å from the former and 1·637 (1) Å from the latter. The overall molecular structure is very similar to that reported for the η^6-C_6H_6 analogue by Garcia *et al.* (1985).

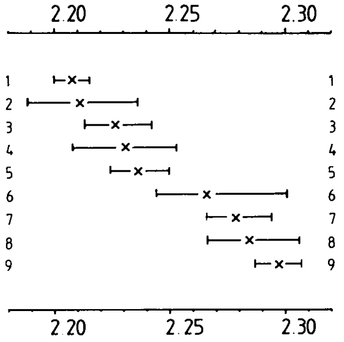

Fig. 2. The range of observed values (⊢⊣) and the mean values (X) of the ruthenium—carbon distances (Å) within the $\{Ru(\eta^6\text{-}C_6Me_6)\}$ moiety in reported polyhedral ruthenaborane species. Numbers 1, 2, 3, *etc.*, refer to the order of the entries in Table 3.

One reason for using the C_6Me_6 ligand is to provide comparison data for ruthenium—carbon distances in the $Ru(\eta^6\text{-}C_6Me_6)$ moiety for a variety of polyhedral ruthenium–boron compounds as gathered in Table 3 and illustrated in Fig. 2. Fewer comparisons are available for the $Ru(C_6H_6)$ moiety. It is of interest that there is statistically significant variation in the mean values, and that this correlates reasonably well with cluster types, shorter ruthenium—carbon distances being generally associated with the more stable *closo*- and conventional *nido*-type clusters, and longer distances being generally associated with the more unusual *nido*-type clusters and open *arachno* cluster types. Obviously it would be useful to have more extensive comparison data, but there would seem to be an implication that additional electron density from the ruthenium centre may be needed for the more open types of clusters, and that this is diverted into the cluster at the expense of ruthenium—carbon bonding.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52547 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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References

Baše, K., Bown, M., Štíbr, B., Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D. & Thornton-Pett, M. (1988). *J. Chem. Soc. Chem. Commun.* pp. 1240–1241.

Bown, M., Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D. & MacKinnon, P. I. (1987). *J. Chem. Soc. Chem. Commun.* pp. 817–818.

Bown, M., Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D., MacKinnon, P. I. & Thornton-Pett, M. (1987). *Organometallics*, **6**, 2254–2256.

Bown, M., Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D. & Thornton-Pett, M. (1986). *J. Organomet. Chem.* **315**, C1–C4.

Bown, M., Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D. & Thornton-Pett, M. (1987*a*). *J. Chem. Soc. Dalton Trans.* pp. 925–930.

Bown, M., Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D. & Thornton-Pett, M. (1987*b*). *J. Chem. Soc. Dalton Trans.* pp. 1169–1174.

Bown, M., Jelínek, J., Štíbr, S., Heřmánek, S., Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D. & Thornton-Pett, M. (1988). *J. Chem. Soc. Chem. Commun.* pp. 974–975.

Bown, M., Plešek, J., Baše, K., Štíbr, B., Fontaine, X. L. R., Greenwood, N. N. & Kennedy, J. D. (1989). *Magn. Reson. Chem.* **27**, 947–949.

Bown, M. & Thornton-Pett, M. (1986). Unpublished work, Univ. of Leeds, England.

Garcia, M. P., Green, M., Stone, F. G. A., Sommerville, R. G., Welch, A. J., Briant, C. K., Cox, D. N. & Mingos, D. M. P. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2343–2348.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

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Structure of 1-Butene(trimethylphosphine)zirconocene

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Abstract. (η-1-Butene)bis(η-cyclopentadienyl)(trimethylphosphine)zirconium, $[Zr(C_5H_5)_2(C_4H_8)\{P(CH_3)_3\}]$, $C_{17}H_{27}PZr$, $M_r = 353{\cdot}6$, orthorhombic, $Pca2_1$, $a = 27{\cdot}946\ (8)$, $b = 8{\cdot}733\ (1)$, $c = 14{\cdot}462\ (3)$ Å, $V = 3529\ (1)$ Å^3, $T = 293$ K, $Z = 8$, $D_x = 1{\cdot}33$ g cm^{-3}, $F(000) = 1472$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 6{\cdot}89$ cm^{-1}, final $R = 0{\cdot}046$ ($wR = 0{\cdot}050$) for 3295 unique observed reflections. The C=C bond of the coordinated butene ligand is coplanar with the P and Zr atoms and this plane approximately bisects the angle made by the planes of the two cyclopentadienyl ligands. There are two molecules in the asymmetric unit which differ only in the conformation of the butene ligand.

Introduction. The title compound (1) is prepared in *ca* 83% yield from zirconocene dichloride with two equivalents of *n*-butyllithium and trimethylphosphine (Buchwald, Watson & Huffman, 1987; Binger, Müller, Benn, Rufinska, Gabor, Krüger & Betz, 1989; Takahashi, Murakami, Kunishige, Saburi, Uchida, Kozawa, Uchida, Swanson & Negishi, 1989). Subsequent reactions of (1) with other alkynes and alkenes such as ethylene and styrene result in substitution of the butene and indicate that this compound is an ideal starting material for synthesizing other alkene– or alkyne–zirconocene complexes. The structures of ethylene(trimethylphosphine)zirconocene and styrene(trimethylphosphine)-zirconocene have already been reported (Binger *et al.*, 1989) as well as that of stilbene(trimethylphosphine)zirconocene (Takahashi *et al.*, 1989). Here we describe the structure of 1-butene(trimethylphosphine)zirconocene and compare it with the structures of the other known alkene derivatives.

Experimental. Crystals of the title compound were grown as dark brown prisms from pentane solution. The crystal chosen for data collection was 0·47 × 0·47 × 0·47 mm. The unit-cell parameters were obtained by a least-squares fit to the θ values of 77 automatically centred reflections ($16{\cdot}6 < \theta < 20{\cdot}8°$). 4577 intensity data ($0 < h < 36$, $0 < k < 10$, $0 < l < 18$) were measured within the range $1{\cdot}41 < \theta < 27{\cdot}32°$ on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ X-radiation by a θ–2θ scan technique in 48 steps, where the time spent measuring the background was half that taken

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