Experimental

The synthesis of $[ZnCl_2(mpit)_2]$ has been reported elsewhere (Williams *et al.*, 1994). Crystals suitable for study were obtained by slow evaporation from CH_2Cl_2.

Crystal data

$[ZnCl_2(C_7H_{10}N_2S)_2]$
$M_r = 444.73$
Monoclinic
$P2_1/n$
$a = 14.0082\ (8)$ Å
$b = 10.803\ (1)$ Å
$c = 14.581\ (1)$ Å
$\beta = 116.625\ (8)°$
$V = 1972.6\ (4)$ Å^3
$Z = 4$
$D_x = 1.50$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.61–14.74°$
$\mu = 1.73$ mm^{-1}
$T = 295$ K
Parallelepiped
0.23 × 0.21 × 0.20 mm
Colorless

Data collection

Rigaku AFC-7 diffractometer
$\omega–2\theta$ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1991)
$T_{min} = 0.38$, $T_{max} = 0.71$
3833 measured reflections
3467 independent reflections

1935 reflections with $F > 6\sigma(F)$
$R_{int} = 0.020$
$\theta_{max} = 25°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 13$
$l = -17 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: ±2%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.044$
$S = 1.85$
1935 reflections
209 parameters
H atoms calculated; $U_H = 0.147\ (9)$ Å^2

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: none
Scattering factors from Cromer & Waber (1974)

Table 1. *Selected geometric parameters (Å, °)*

Zn(1)—Cl(1)	2.264 (3)	Zn(1)—S(2)	2.370 (2)
Zn(1)—Cl(2)	2.254 (2)	S(1)—C(1)	1.719 (6)
Zn(1)—S(1)	2.374 (3)	S(2)—C(8)	1.708 (9)
Cl(1)—Zn(1)—Cl(2)	109.9 (1)	Cl(2)—Zn(1)—S(2)	113.0 (1)
Cl(1)—Zn(1)—S(1)	113.7 (1)	S(1)—Zn(1)—S(2)	102.8 (1)
Cl(2)—Zn(1)—S(1)	110.7 (1)	Zn(1)—S(1)—C(1)	96.3 (3)
Cl(1)—Zn(1)—S(2)	106.6 (1)	Zn(1)—S(2)—C(8)	99.3 (2)

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically and H atoms were generated with ideal geometries (C—H = 0.96 Å) and refined with a group displacement parameter as riding groups.

Data collection: Rigaku AFC-7 software. Cell refinement: Rigaku AFC-7 software. Data reduction: *TEXSAN* (Swepston, 1993). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *SHELXTL-Plus* (Sheldrick, 1991). Molecular graphics: *SHELXTL-Plus*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1301). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The *isonido*-Metalladicarbaborane [1,1,1-H{P(CH$_3$)$_3$}$_2$-6-Cl-1,2,4-IrC$_2$B$_8$H$_9$]

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Abstract

A single-crystal diffraction study of the title iridadicarbaundecaborane species, 6-chloro-1,1-bis(trimethylphosphine-*P*)-1-*endo*-H-2,3-dicarba-1-irida-*isonido*-undecaborane(12), $[IrH(PMe_3)_2(C_2B_8H_9Cl)]$ or $[(PMe_3)_2(H)IrC_2B_8H_9Cl]$, shows that it has an *isonido*-type structure with a four-membered Ir1–C2–C4–B7 open face. The presence of the chlorine substituent on vertex B6 suggests that the compound is formed *via* a simple ligand elimination and intrafacial addition of the metal vertex to a neighbouring boron vertex in the probable precursor compound *nido*-$[(PMe_3)_2(CO)IrC_2B_8H_{10}Cl]$.

Comment

In the course of our investigations of heteroatom additions to metallaborane clusters to give metalla-

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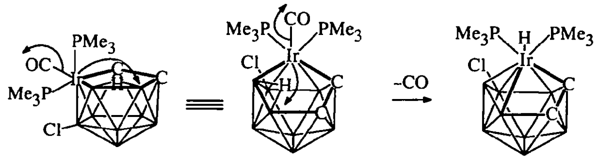
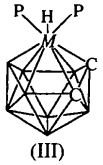
heteroboranes, we isolated a small amount of the title chloro-substituted iridadicarbaundecaborane cluster, (II) (Fig. 1), which was prepared as described in the *Experimental* section. The characterization of one of the two products obtained, *nido*-[9,9,9-$(PMe_3)_2(CO)$-5-Cl-9,7,8-$IrC_2B_8H_{10}$], (I), is discussed elsewhere (Bould, Rath & Barton, 1996), but the second, with its yellow dagger-shaped crystals, which amounted to *ca* 30–40% of the total yield as estimated by ^{11}B NMR spectroscopy, was characterized by a single-crystal X-ray diffraction study, the details of which are presented here.



(I) (II)



(III)

The cluster is observed to be of the *isonido* type, similar to the triphenylphosphine-ligated analogue [$(PPh_3)_2$-$HIrC_2B_8H_{10}$] first synthesized by Jung & Hawthorne (1980) directly from [$IrCl(PPh_3)_3$] and $NaC_2B_8H_{11}$, and described from the NMR data as a fully closed species, (III), but which was subsequently shown by Thornton-Pett & Kennedy (Nestor *et al.*, 1989) to contain a four-membered Ir1–C2–C4–B7 open face. The principal feature of the compound described here, in addition to the presence of the open face, is the position of the chlorine substituent on the B6 vertex. It acts as a label and indicates that compound (II) may be derived directly from the co-product (I) through elimination of the CO group on iridium and partial cluster closure *via* addition of the metal vertex across the open face of the cluster with concomitant bridging H-atom migration to the iridium (see scheme above). In the rhodium analogue, [$(PEt_3)_2HRhC_2B_8H_{10}$], which has a coordinatively unsaturated metal vertex, this process appears to be reversible (Jung & Hawthorne, 1980). Direct thermolysis of the unsubstituted analogue of compound (II) has been shown to give the corresponding *isonido* compound in *ca* 25% yield (Bould, Rath & Barton, 1996).

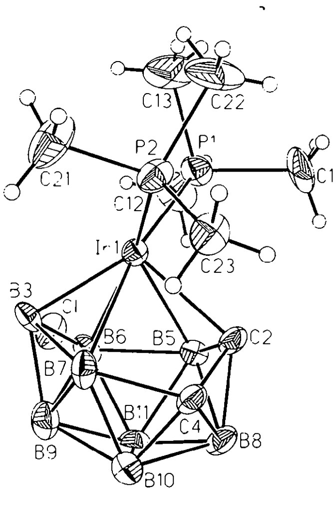


Fig. 1. View of one of the two unique molecules of (II) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

The structural features of compound (II) are comparable to those of the unsubstituted cage species [$(PPh_3)_2$-$HIrC_2B_8H_{10}$] reported previously (Nestor *et al.*, 1989). The shape of the four-membered open face (Ir1–C2–C4–B7) is almost identical in the two species, the averages of the angles at the four corners for the two molecules of (II) being 97.3 (7), 108.2 (9), 82.6 (5) and 70.2 (5)° for C2, C4, B7 and Ir1, respectively, and for [$(PPh_3)_2HIrC_2B_8H_{10}$] they are 96.3 (4), 107.2 (5), 84.8 (4) and 69.1 (3)°, respectively. The Ir···C4 and C2···B7 non-bonded distances across the face are 2.80 and 2.64 Å, respectively, in (II) and 2.78 and 2.58 Å in [$(PPh_3)_2HIrC_2B_8H_{10}$]. This is in accord with the slightly longer distances in the face of (II) relative to those in the unsubstituted cage. It appears that the influence of the chlorine substituent in (II) results in a slight increase in the cage interatomic distances.

The confirmation of compound (II) as an *isonido* species with an open-square face adds to the number of examples of what may be considered structurally to be 'frozen' intermediates or transition states proposed (Kleier, Dixon & Lipscomb, 1978) for the known fluxional process which renders all the vertices in closed 11-vertex boranes and carbaboranes equivalent on the NMR timescale (Tolpin & Lipscomb, 1973; Weirsema & Hawthorne, 1973). The process is thought to involve diamond–square–diamond rearrangements and the square-faced species is the transition state for such processes. Compound (II) adds to the number of *isonido*-11-vertex clusters with an open-square face, which also includes [1-(η^6-MeC_6H_4-^iPr)-2,4-Me_2-1,2,4-$RuC_2B_8H_8$] (Bown, Fontaine, Greenwood, Kennedy & Thornton-Pett, 1987) and supports the proposal (Kennedy & Štíbr, 1994) that structural relationships and patterns also exist for the growing number of known systems which appear not to conform either to the well established 'conventional' electron-counting or structural rules (Wade, 1976; Williams, 1976).

Experimental

Acetylene, direct from a cylinder after passing through a trap at 195 K, was bubbled through a xylene solution of 25 mg of *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{11}Cl$] (Bould, Greenwood & Kennedy, 1984), contained in a round-bottomed flask with a sidearm fitted with a reflux condenser, for 5 min before the solution was heated strongly to reflux for 40 min with a continuous flow of acetylene. The mixture was allowed to cool and the solvent removed on a Schlenk line, redissolved in CH_2Cl_2, filtered and the filtrate applied to a preparative thin-layer chromatography plate (20 × 20 cm glass plates coated with 0.1 cm of Aldrich standard grade silica gel with gypsum binder and fluorescent indicator) and developed using 60% CH_2Cl_2/pentane as the mobile phase. A single band, observed under UV light, at R_f 0.3 contained 14.5 mg of material. The band was examined by NMR and observed to be a mixture of two principal compounds which could not be further chromatographically separated. However, crystallization from pentane/CH_2Cl_2 gave two species in the form of clumps of well formed yellow crystals of the title compound surrounded by colourless thin stacked platelets of *nido*-[$(PMe_3)_2(CO)IrC_2B_8H_{10}Cl$], the characterization of which will be described elsewhere (Bould *et al.*, 1996). A crystal of (II) suitable for a single-crystal X-ray diffraction study was obtained using a microscope by manually removing the yellow crystals from the clumps.

Crystal data

[$IrH(C_3H_9P)_2(C_2B_8H_9Cl)$]
$M_r = 500.37$
Monoclinic
$P2_1/c$
$a = 9.639\,(2)$ Å
$b = 16.346\,(2)$ Å
$c = 24.1086\,(14)$ Å
$\beta = 90.563\,(9)°$
$V = 3798.6\,(8)$ Å^3
$Z = 8$
$D_x = 1.750$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 5.06–12.50°$
$\mu = 7.321$ mm^{-1}
$T = 295\,(2)$ K
Long needle
0.30 × 0.10 × 0.06 mm
Light yellow

Data collection

Siemens *P4RA* diffractometer
ω scans
Absorption correction: empirical from ψ scans (*XEMP* in *SHELXTL-Plus*; Sheldrick, 1994)
$T_{\min} = 0.507$, $T_{\max} = 0.645$
10 998 measured reflections
8733 independent reflections

5015 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 27.5°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 21$
$l = -31 \rightarrow 31$
3 standard reflections every 97 reflections intensity decay: 17%

Refinement

Refinement on F^2
$R(F) = 0.062$
$wR(F^2) = 0.137$
$S = 1.024$
8731 reflections
361 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.005$
$\Delta\rho_{\max} = 1.73$ e Å^{-3}
$\Delta\rho_{\min} = -0.97$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for compound (II)*

	Molecule 1	Molecule 2
Ir1—B3	2.054 (12)	2.086 (14)
Ir1—C2	2.183 (11)	2.165 (12)
Ir1—P2	2.308 (3)	2.316 (3)
Ir1—P1	2.319 (3)	2.318 (3)
Ir1—B6	2.330 (14)	2.31 (2)
Ir1—B5	2.341 (14)	2.32 (2)
Ir1—B7	2.40 (2)	2.429 (14)
Cl—B6	1.83 (2)	1.86 (2)
C2—C4	1.50 (2)	1.50 (2)
C2—B5	1.66 (2)	1.65 (2)
C2—B8	1.72 (2)	1.74 (2)
B3—B9	1.75 (2)	1.78 (2)
B3—B6	1.78 (2)	1.74 (2)
B3—B7	1.81 (2)	1.81 (2)
C4—B10	1.67 (2)	1.64 (2)
C4—B8	1.72 (2)	1.71 (2)
C4—B7	1.76 (2)	1.75 (2)
B5—B8	1.82 (2)	1.82 (2)
B5—B11	1.84 (2)	1.83 (2)
B5—B6	1.86 (2)	1.87 (2)
B6—B9	1.75 (2)	1.78 (2)
B6—B11	1.81 (2)	1.81 (2)
B7—B10	1.87 (2)	1.84 (2)
B7—B9	1.92 (2)	1.91 (2)
B8—B11	1.75 (2)	1.73 (2)
B8—B10	1.78 (2)	1.77 (2)
B9—B10	1.78 (2)	1.78 (2)
B9—B11	1.78 (2)	1.79 (2)
B10—B11	1.78 (2)	1.79 (2)
B3—Ir1—C2	106.8 (5)	107.1 (6)
B3—Ir1—P2	12.7 (4)	120.5 (4)
C2—Ir1—P2	96.6 (3)	92.4 (3)
B3—Ir1—P1	135.4 (4)	134.0 (4)
C2—Ir1—P1	99.4 (3)	100.7 (4)
P2—Ir1—P1	99.00 (13)	93.59 (12)
B3—Ir1—B6	47.3 (5)	46.4 (6)
C2—Ir1—B6	82.9 (5)	83.5 (5)
P2—Ir1—B6	157.6 (4)	163.0 (4)
P1—Ir1—B6	103.2 (4)	103.4 (4)
B3—Ir1—B5	89.4 (5)	89.6 (6)
C2—Ir1—B5	42.8 (5)	43.0 (5)
P2—Ir1—B5	139.1 (4)	133.9 (4)
P1—Ir1—B5	85.9 (3)	86.5 (4)
B6—Ir1—B5	47.0 (5)	47.8 (6)
B3—Ir1—B7	47.1 (5)	46.5 (5)
P2—Ir1—B7	88.8 (4)	94.4 (4)
P1—Ir1—B7	167.6 (4)	168.3 (4)
B6—Ir1—B7	69.9 (5)	68.6 (5)
B5—Ir1—B7	81.9 (5)	81.8 (5)
C4—C2—B5	110.4 (10)	109.0 (11)
C4—C2—B8	63.9 (8)	63.0 (9)
B5—C2—B8	64.9 (8)	64.8 (9)
B5—C2—Ir1	73.7 (6)	73.4 (7)
B8—C2—Ir1	122.1 (8)	121.4 (9)
C2—C4—B10	115.6 (11)	117.7 (11)
C2—C4—B8	64.3 (8)	65.4 (9)
B10—C4—B8	63.6 (9)	63.8 (9)
B10—C4—B7	65.9 (8)	65.6 (8)
B8—C4—B7	114.9 (10)	115.3 (10)
Cl—B6—B5	118.9 (9)	117.4 (10)
B9—B6—Ir1	100.7 (9)	103.1 (9)
B11—B6—Ir1	111.0 (8)	111.0 (9)
Cl—B6—Ir1	126.1 (7)	128.3 (8)
B5—B6—Ir1	66.8 (6)	66.4 (6)
C4—B7—B3	129.2 (10)	128.3 (11)
C4—B7—B10	54.7 (7)	54.3 (8)
B3—B7—B10	108.9 (11)	110.2 (10)
C4—B7—B9	103.0 (10)	103.2 (10)
B3—B7—B9	55.9 (8)	57.2 (8)
B10—B7—B9	56.0 (8)	56.6 (8)
B3—B7—Ir1	56.3 (6)	56.7 (6)
B10—B7—Ir1	111.3 (9)	110.9 (8)
B9—B7—Ir1	93.4 (8)	94.9 (8)

C4—B8—C2	51.9 (7)	51.6 (7)
C4—B8—B11	103.7 (9)	103.2 (11)
C2—B8—B11	107.0 (10)	106.9 (11)
C4—B8—B10	56.9 (8)	56.2 (8)
C2—B8—B10	99.9 (9)	100.0 (10)
C4—B8—B5	94.7 (9)	93.3 (10)
C2—B8—B5	55.8 (7)	55.1 (8)
B10—B8—B5	102.6 (10)	103.4 (12)
C4—B10—B11	104.8 (11)	103.5 (10)
C4—B10—B9	113.4 (11)	114.1 (11)
B11—B10—B7	104.4 (11)	103.8 (10)

The title structure was solved by the Patterson method and refined by full-matrix least-squares techniques. The non-H atoms were refined anisotropically to convergence. The methyl H atoms were treated using a riding model. Neither the borane H atoms nor the hydride ligand were included in the model.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1240). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis{μ-[1-(*N*-methylsulfonimidoyl)-2,2-diphenylethene]}-$1\kappa^2C^1$,*N*:$2\kappa O$;$1\kappa O$:-$2\kappa^2C^1$,*N*-bis[(tetrahydrofuran-*O*)lithium] Tetrahydrofuran Solvate and 1-(*N*-Methylphenylsulfonimidoyl)-2,2-diphenylethene

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Abstract

The crystal structure of the THF (C_4H_8O) solvate of $[Li_2(C_{21}H_{19}NOS)_2(C_4H_8O)_2]$, (1), prepared by the addition of *n*-BuLi to 1-(*N*-methylphenylsulfonimidoyl)-2,2-diphenylethene, $C_{21}H_{19}NOS$, (2), at low temperature in THF, shows a centrosymmetric dimeric aggregate featuring an eight-membered ring with the atomic sequence (Li—C—S—O)$_2$. The O atom of one tetrahydrofuran molecule, the sulfoximine O and N atoms, and the C_α atom are coordinated to the lithium cation in a distorted tetrahedral arrangement. A comparison with the molecular structure of the precursor (2) is drawn.

Comment

In recent years, sulfoximines and their derivatives have become increasingly important in asymmetric synthesis (Johnson, 1985). The stabilization of carbanionic sites adjacent to the sulfonimidoyl moiety has allowed the use of such lithiated derivatives for the transfer of chiral information (Gais, Erdelmeier & Lindner, 1986). Despite their widespread synthetic use, remarkably little is known about the structures of such lithio derivatives and no solid-state data exist for the synthetically important lithiovinyl carbanions (Gais, Erdelmeier, Lindner & Vollhardt, 1986; Chassaing & Marquet, 1978). Such data are required for a detailed understanding of the mechanism in stereoselective C—C bond formation reactions. In principle, three chelating lithium-binding modes are possible in lithiovinylsulfoximines, resulting in *N*,*C*-, *O*,*C*- or *O*,*N*-chelates. In this paper, we describe the