

Two iridanonaborane compounds

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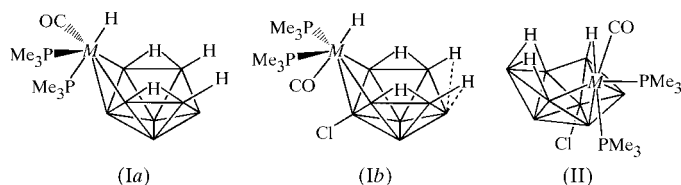
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Two iridanonaborane compounds, 4-carbonyl-5,6,8,9-bis- μ H-4-hydrido-4-bis(trimethylphosphine)-4-irida-*arachno*-nonaborane(12), [IrH(B₈H₁₂)(C₃H₉P)₂(CO)], (Ia), and 2-carbonyl-2,5:6,9:8,9-tri- μ H-4-chloro-2-bis(trimethylphosphine)-2-iridano-*nido*-nonaborane(11), [Ir(B₈H₁₀Cl)(C₃H₉P)₂(CO)], (II), are described. Compound (II) shows evidence of effective chlorine-substituent migration during its formation.

Comment

The *arachno*-iridanonaborane [4,4,4,4-CO(PMe₃)₂H-*arachno*-4-IrB₈H₁₂], (Ia), and its chloro analogue [4,4,4,4-(CO)(PMe₃)₂H-*arachno*-4-IrB₈H₁₁-2-Cl], (Ib), were obtained from the reaction of [IrCl(CO)(PMe₃)₂] with the *nido*-[B₉H₁₂][−] anion (Bould *et al.*, 1982, 1984). In the original reports on these compounds, the *arachno* structural type was characterized by a single-crystal X-ray diffraction analysis of the chlorinated derivative, (Ib), but the data were of insufficient quality for H-atom location, although they were reasonably positioned from the results of NMR spectroscopy. In the report on the structure of (Ib), it was surmised that the two *endo*-terminal H atoms may have partial bridging character (hatched lines in the scheme). However, recent experimental observations and theoretical considerations on non-metal-containing *arachno* nine-vertex species (Hofmann & Schleyer, 1999; Bould *et al.*, 2001) suggest that one of these H atoms may be bridging and one *endo*-terminal, with rapid equilibration between the two in solution, and it is useful to attempt to investigate their character crystallographically.



Compound (Ib) has the symmetric ligand disposition shown in the Scheme above. The structural determination of (Ia)

(Fig. 1) now confirms that it has the alternative asymmetric ligand disposition reasonably proposed from NMR spectroscopy. Otherwise, interatomic dimensions in (Ia) are very similar to those in (Ib), with the main differences arising principally from metal hydride *trans* effects. Thus, the Ir4–P2 distance of 2.368 (2) Å *trans* to the hydride in (Ia) is significantly longer than the *cis*-to-H Ir4–P distances in (Ib) [2.334 (2) and 2.346 (2) Å] and Ir4–P1 in (Ia) [2.3319 (15) Å]. Although the Cl substituent on B2 has a noticeable effect on the thermodynamic parameters for the *arachno* → *nido* closure process (Bould *et al.*, 1984), its absence in (Ia) has no significant effect on the interatomic dimensions regarding vertex B2 when compared with (Ib). Unfortunately, the H atoms did not refine satisfactorily and their disposition as *endo*-terminal or bridging remains unresolved in nine-vertex *arachno*-metallanonaborane clusters.

The *arachno* nine-vertex iridaboranes are also interesting starting materials for a variety of interesting metallaborane chemistry (Bould *et al.*, 1996, 1997). Fusion of *arachno* metallanonaboranes in molten decaborane affords a number of interesting fused macropolyhedral species (Bould *et al.*, 1999). For example, compound (Ia) gives the mixed cluster fusion products [(PMe₃)₂IrB₂₆H₂₄Ir(CO)(PMe₃)₂] and [(CO)(PMe₃)₂IrB₁₇H₂₀] in low yields. In an attempt to vary these yields and products, we have used the chloro-substituted species, (Ib). In the event, however, fusion of an intimate mixture of decaborane(14) and (Ib) at 396 K afforded the second title compound, [2,2,2-(CO)(PMe₃)₂-*nido*-2-IrB₈H₁₀-4-Cl], (II), as the only isolable product. A single-crystal X-ray diffraction study was carried out in order to confirm the position of the Cl substituent deduced from NMR spectroscopy (see *Experimental*).

All atoms, including H atoms, were located and freely refined in reasonable positions for (II) (Fig. 2). Additionally, the position of the Cl substituent is confirmed. It differs from the position previously reported for [2,2,2-(CO)(PMe₃)₂-*nido*-2-IrB₈H₁₀-3-Cl] obtained from the thermolysis of (Ib) in the absence of B₁₀H₁₄ (Bould *et al.*, 1984). The cluster is also similar to the other structurally characterized *nido*-metalla-

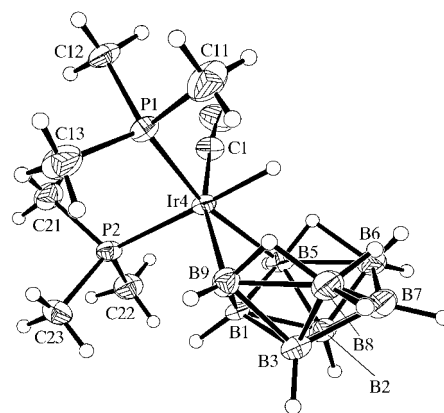


Figure 1

A perspective view of a single molecule of (Ia) drawn with 40% probability displacement ellipsoids and with H atoms shown as small circles of arbitrary radii.

nonaborane species, namely, the third-row rhenaborane [(PMe₂Ph)₃H₂-*nido*-ReB₈H₁₁] (Beckett *et al.*, 1988), in which all H atoms were located except for the terminal and bridging metal hydrides, and the *nido*-[IrB₈] subcluster in the macropolyhedral species [(PMe₃)₂IrB₂₆H₂₄Ir(CO)(PMe₃)₂] (Bould *et al.*, 1997).

The position of the Cl substituent in (II) indicates that, during the thermolysis of the *arachno*-metallaborane precursor compound (*Ib*) to give (II), the substituent has moved from a B vertex adjacent to the metal atom in the precursor to a position one vertex removed from the metal. In this context, it may be noted that strong heating of a xylene solution of [2,2,2-(CO)(PMe₃)₂-*nido*-2-IrB₈H₁₀-3-Cl] results in cluster closure, to give the *isocloso* species [(PMe₃)₂HIrB₈H₇Cl] in which a comparable movement of the Cl to a B vertex remote from the metal centre has been noted (Bould *et al.*, 1982). A mechanism was proposed in which the migration would occur *via* a cluster diamond-square-diamond rearrangement during the *nido* → *isocloso* step. The low yield in the precursive *arachno* → *nido* closure reported here makes the proposal of a reaction mechanism speculative, although it does suggest that the Cl-migration step could also possibly occur prior to the *nido* → *isocloso* closure.

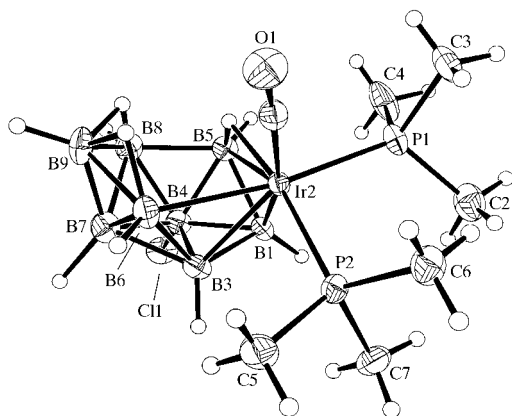


Figure 2
A perspective view of a single molecule of (II) drawn with 40% probability displacement ellipsoids and with H atoms shown as small circles of arbitrary radii.

Experimental

The previously reported *arachno* compounds (*Ia*) and (*Ib*) were prepared as described by Bould *et al.* (1984). Single crystals of (*Ia*) were obtained by diffusion of pentane through a benzene layer into a CDCl₃ solution of the compound. The previously unreported *nido* compound, (II), was isolated following thermolysis of the *arachno* compound (*Ib*) as follows: a finely ground mixture of [4,4,4,4-(CO)(PMe₃)₂H-4-IrB₈H₁₁-2-Cl] [(*Ib*), 73 mg, 145 μmol] and B₁₀H₁₄ (0.51 g, 4200 μmol) was placed in a 10 mm soda-glass NMR tube which was then evacuated, refilled with nitrogen and heated in an oil bath at 396 K for 55 min, after which time, the excess B₁₀H₁₄ was removed by sublimation (357 K, *ca* 0.01 mm Hg; 1 mm Hg = 133.322 Pa). Thin-layer chromatography of the residue (Aldrich standard grade silica gel with gypsum binder and fluorescent

indicator, 70:30 CH₂Cl₂/hexane) showed a number of diffuse faint yellow after and red bands between *R_F* 0.1 and 0.8. Separation and identification of these bands proved difficult, but one yellow band, at *R_F* 0.1, further separation by high-performance liquid chromatography [silica, Lichosorb Si60 7 μm, 260 × 16 mm column, CH₂Cl₂/hexane (80:20, 5 ml min⁻¹), *R_T* 15 min] and crystallization by diffusion of pentane through a benzene layer into a CDCl₃ solution of the compound, gave crystals of (II) suitable for diffraction analysis (2 mg, 4 μmol, 3%). NMR spectroscopic analysis: p.p.m., CDCl₃, 300 K, Bruker 250 ARX spectrometer, δ(¹¹B) [δ(¹H) in square brackets]: B1 +19.9 [+4.77], B4 +19.9 (site of Cl substituent), B6 -4.8 [+3.01], B(3, B8, B9) {-12.2 [-1.35], -14.2 (2B) [-2.8, -1.30]}, B5 -35.8 [+0.14], B7 -51.7 [-1.11]; ¹H NMR (δ, p.p.m.): H2/H5 -14.46 [²J(³¹P-¹H) 62 Hz], H6/H9 and H8/H9 -2.76 and -2.02, P(CH₃)₃ +1.91 and +1.78 [²J(³¹P-¹H) 10 Hz]; ³¹P NMR (δ, p.p.m.): -42.0 and -51.5.

Compound (Ia)

Crystal data

[IrH(B₈H₁₂)(C₃H₉P)₂(CO)]
M_r = 471.94
Monoclinic, *P*2₁/*n*
a = 9.2035 (2) Å
b = 15.9788 (5) Å
c = 13.2013 (3) Å
β = 99.670 (2)°
V = 1913.81 (8) Å³
Z = 4

D_x = 1.638 Mg m⁻³
Mo *K*α radiation
Cell parameters from 11 332 reflections
θ = 1.00–27.48°
μ = 7.128 mm⁻¹
T = 150 (2) K
Prism, colourless
0.62 × 0.25 × 0.11 mm

Data collection

Nonius KappaCCD area-detector diffractometer
1° φ scans for χ = 0° and scans for χ = 90°
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
T_{min} = 0.096, *T_{max}* = 0.508
15 922 measured reflections

3737 independent reflections
3547 reflections with *I* > 2σ(*I*)
R_{int} = 0.075
θ_{max} = 26°
h = -11 → 11
k = -19 → 19
l = -16 → 16

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.041
wR (*F*²) = 0.105
S = 1.097
3737 reflections
179 parameters
H atoms constrained

w = 1/[σ²(*F_o*²) + (0.0588*P*)² + 4.8183*P*]
where *P* = (*F_o*² + 2*F_c*²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 2.01 e Å⁻³
Δρ_{min} = -2.88 e Å⁻³
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.0037 (5)

Table 1

Selected geometric parameters (Å, °) for (*Ia*).

Ir4—C1	1.883 (6)	Ir4—P1	2.3319 (15)
Ir4—B1	2.251 (6)	Ir4—P2	2.368 (2)
Ir4—B9	2.272 (8)	C1—O1	1.143 (7)
Ir4—B5	2.285 (6)		
C1—Ir4—B1	129.4 (3)	B5—Ir4—P1	163.4 (2)
C1—Ir4—B9	166.2 (3)	C1—Ir4—P2	92.5 (2)
B1—Ir4—B9	46.6 (3)	B1—Ir4—P2	81.5 (2)
C1—Ir4—B5	86.0 (2)	B9—Ir4—P2	99.3 (2)
B9—Ir4—B5	85.1 (2)	B5—Ir4—P2	99.0 (2)
C1—Ir4—P1	97.9 (2)	P1—Ir4—P2	96.96 (5)
B1—Ir4—P1	132.7 (2)	O1—C1—Ir4	175.7 (6)
B9—Ir4—P1	87.9 (2)		

Compound (II)

Crystal data

[Ir(B₈H₁₀Cl)(C₃H₉P)₂(CO)]
M_r = 504.36
 Monoclinic, *P*2₁/*n*
a = 9.2655 (1) Å
b = 12.1784 (1) Å
c = 16.8668 (1) Å
 β = 94.702 (1)°
V = 1896.83 (3) Å³
Z = 4

D_x = 1.766 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 8192 reflections
 θ = 2–27°
 μ = 7.335 mm⁻¹
T = 223 (2) K
 Rectangular, yellow
 0.23 × 0.22 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (*SADABS*; Blessing, 1995)
T_{min} = 0.283, *T_{max}* = 0.528
 55 769 measured reflections

4150 independent reflections
 3824 reflections with *I* > 2σ(*I*)
R_{int} = 0.038
 θ_{\max} = 27°
h = -11 → 11
k = -15 → 15
l = -21 → 21

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.017
wR(*F*²) = 0.041
S = 1.167
 4150 reflections
 221 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.012P)^2 + 2.6P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.00 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{Å}^{-3}$

Table 2

Selected geometric parameters (Å, °) for (II).

Ir2—C1	1.930 (3)	Ir2—P1	2.3578 (8)
Ir2—B1	2.156 (3)	Ir2—B5	2.491 (3)
Ir2—B3	2.291 (3)	Cl1—B4	1.823 (3)
Ir2—P2	2.3174 (8)	O1—C1	1.142 (4)
Ir2—B6	2.323 (3)		
C1—Ir2—B1	165.75 (13)	B1—Ir2—P1	89.51 (9)
C1—Ir2—B3	129.64 (13)	B3—Ir2—P1	134.20 (9)
B1—Ir2—B3	46.39 (13)	P2—Ir2—P1	95.31 (3)
C1—Ir2—P2	89.72 (9)	B6—Ir2—P1	169.84 (9)
B1—Ir2—P2	102.81 (9)	C1—Ir2—B5	122.37 (12)
B3—Ir2—P2	85.48 (9)	B1—Ir2—B5	44.33 (12)
C1—Ir2—B6	84.04 (13)	B3—Ir2—B5	67.93 (11)
B1—Ir2—B6	88.10 (13)	P2—Ir2—B5	146.78 (8)
B3—Ir2—B6	46.72 (13)	B6—Ir2—B5	81.49 (12)
P2—Ir2—B6	94.85 (9)	P1—Ir2—B5	89.90 (8)
C1—Ir2—P1	96.16 (9)	O1—C1—Ir2	177.0 (3)

Methyl H atoms were constrained to calculated positions with isotropic displacement parameters equal to 1.2*U_{eq}* of the parent C atom. Cluster-associated H atoms were located *via* Fourier difference syntheses and were included in structure-factor calculations but were not refined. For both compounds, all boron-cage H atoms were

located from the difference Fourier map and for (Ia), they were not refined, and for (II), they were refined freely [B—H 1.07 (4)–1.39 (4) Å]. Non-boron-cage H atoms were included in their idealized geometry and were treated with the appropriate riding model (*AFIX* in *SHELXTL*; Sheldrick, 1998). In (Ia), the maximum and minimum electron-density peaks are located 0.92 and 0.85 Å, respectively, from the Ir4 atom. For (II), the maximum electron-density peak is 0.90 Å from the Ir2 atom.

For compound (Ia), data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

For compound (II), data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97*; program(s) used to refine structure: *SHELXL97*; molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1295). Services for accessing these data are described at the back of the journal.

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