# The Crystal and Molecular Structure of [1,1,1,1-(CO)H(PPh$_3$)$_2$-*arachno*-1-IrB$_3$H$_7$] * and some Bonding Considerations in *arachno*-Type Four-vertex Metal 'π-Allyl' and 'Borallyl' Clusters

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The detailed molecular structure of [(CO)(PPh$_3$)$_2$HIrB$_3$H$_7$] has been determined by *X*-ray diffraction analysis. The colourless crystals are monoclinic, space group $P2_1/n$ with $a$ = 1 182.0(3), $b$ = 2 189.4(4), $c$ = 1 355.7(3) pm, β = 104.27(2) °, and $Z$ = 4. The molecular structure ($R$ = 0.032 for 4 119 reflections) features a four-vertex butterfly cluster (IrB$_3$) with Ir on a 'hinge' position. The structure is interpreted in terms of a 'capped octahedral' seven-orbital 18-electron $d^4$ iridium(v) complex in which the metal–borane bonding occurs predominantly *via* three two-electron two-centre iridium–boron bonds. The cluster bonding implications are discussed with reference to the 'π-allyl' and 'borallyl' bonding modes.

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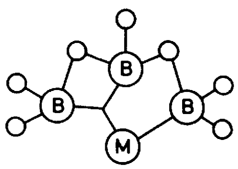
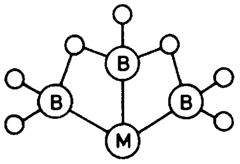
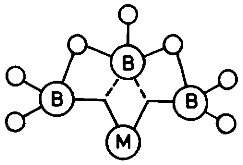
The first examples of the *arachno*-1-metallatetraboranes to be reported were a series of nickel, palladium, and platinum compounds.[1] These were typified by [(PMe$_2$Ph)$_2$PtB$_3$H$_7$] which was examined by single-crystal *X*-ray diffraction analysis.[2] The solution of the structure was beset by severe disorder problems, and the model used to account for the results suggested that the structure was best represented by an asymmetric eight-electron localized σ,$\eta^2$-'borallyl' interpretation as in (I) with a straightforward platinum(II) square-planar bonding geometry. [In structures (I)—(V) the non-borane ligands or groups attached to the metal centre M have been omitted for clarity.] An alternative ten-electron cluster bonding model (II), although feasible, was not considered; indeed a detailed distinction between the two models could not have been drawn at that time since the structure solution was too inexact for the definitive location of the cluster boron and hydrogen atoms.



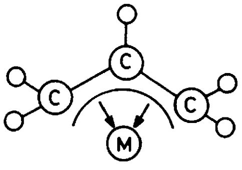
(I)



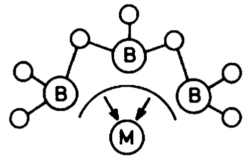
(II)



(III)



(IV)



(V)

The next example to be reported[3] was the iridium compound [(CO)(PPh$_3$)$_2$HIrB$_3$H$_7$], which was interpreted on i.r. and n.m.r. spectroscopic evidence as also having an eight-electron cluster and an essentially octahedral distribution of bonding orbitals about an iridium(III) centre.

We can now discuss this particular compound more thoroughly, as we have succeeded in obtaining crystals suitable for single-crystal *X*-ray diffraction analysis. This gave unequivocal atomic positions, including those of hydrogen, and we report the results of the work here.

## Results and Discussion

The all-atom structure of [(CO)(PPh$_3$)$_2$HIrB$_3$H$_7$] is given in Figure 1, which shows the entire molecular numbering system. Figure 2 shows a different projection of the metallaborane cluster with the phenyl groups omitted for clarity. Selected interatomic distances are given in Table 1, and angles between interatomic vectors in Table 2.

It can be seen that the metallaborane cluster itself (*i.e.* the structure excluding the phenyl groups) conforms closely to idealized mirror-plane symmetry. Comparison between left-hand and right-hand columns in Tables 1 and 2 shows that deviations from this ideal are small, and presumably derive from the different Ir–P and Ir–C bond rotamers for P(1) and P(2) in the solid state and the concomitant asymmetric electronic and crystal packing effects. The symmetric structure is in immediate contrast to the asymmetric one deduced[1,2] for the (disordered) platinum compound [(PMe$_2$Ph)$_2$PtB$_3$H$_7$].

The distances to iridium from the phosphorus and carbonyl carbon atoms are within the ranges of 230—240 and 187—194 pm respectively previously found[4—10] for other contiguous iridaborane species. There are only a few data of limited accuracy for Ir–H(terminal) distances in metallaborane-type species so no real comparisons can be made here. The angles subtended at the iridium atom by the phosphorus, the hydride hydrogen, and carbonyl carbon atoms are in the range 82—99°, suggesting an essentially octahedral geometry in this region. The exception to this is the angle P(1)–Ir(1)–P(2) at 107.5°. A similarly large angle [106.1(1)°] is also observed, for example, in the carbonylbis(phosphine)iridahexaborane [(CO)(PPh$_3$)$_2$IrB$_5$-

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* 1-Carbonyl-1-hydrido-1,1-bis(triphenylphosphine)-*arachno*-1-iridatetraborane.

*Supplementary data available* (No. SUP 56270, 4 pp.): thermal parameters, phenyl H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

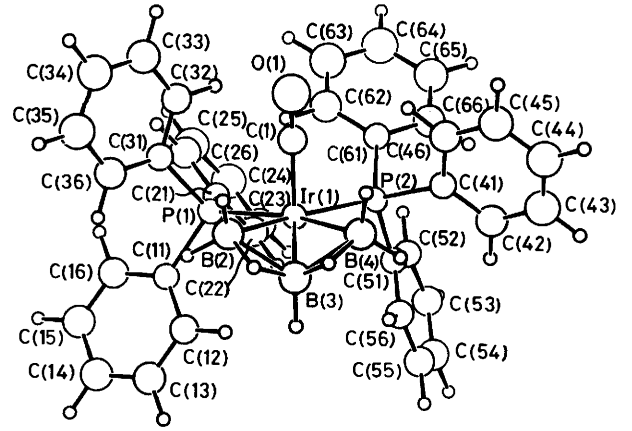


**Figure 1.** ORTEP drawing and numbering scheme of the all-atom molecular structure of $[(CO)(PPh_3)_2HIrB_3H_7]$

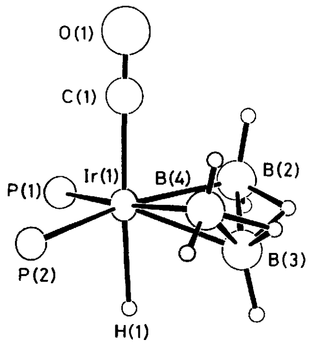


**Figure 2.** Detail of the metallaborane cluster of $[(CO)(PPh_3)_2HIrB_3H_7]$; the phenyl groups have been omitted for clarity

$H_8]$,[4] which also has two mutually *cis* phosphine ligands *trans* to a boron cluster. The large angle may arise from non-bonded interaction of the P-phenyl groups, or from constraint by the borane cluster of the bonding angles *trans* to the phosphines.

The geometry within the *arachno*-$IrB_3H_7$ cluster is largely comparable to the other structurally defined *arachno* four-vertex boron clusters,[11–13] although some deviation is to be expected to accommodate the metal atom. The dihedral butterfly angle is 127°, a value similar to those in $B_4H_{10}$ (117°),[11] $B_5H_9$·tmen (tmen = *NNN'N'*-tetramethylethylenediamine) (*ca.* 129°),[12] and 1-$[F_2(Me_2N)P]B_4H_8$ (137°).[13] The B(3)–B(2,4) distances of 183—184 pm are very similar to those of the ten-electron species $B_4H_{10}$ (184—185 pm),[10] but somewhat larger than those in the eight-electron species $B_5H_9$·tmen (172—179 pm)[12] and 1-$[F_2(Me_2N)P]B_4H_8$ (175—176 pm).[13] In addition, the approximately tetrahedral disposition of the hydrogen atoms about the boron atoms [angles HBH 100(4)—116(4)°] is as expected by comparison with $B_4H_{10}$, $B_5H_9$·tmen, and 1-$[F_2(Me_2N)P]B_4H_8$, and confirms the general structural predictions for the hydrogen atoms in this type of metallaborane made in refs. 1—3 and 14, which were based principally on n.m.r. spectroscopy. The iridium–boron distances of 220 and 230 pm are within the range of 213—246 pm observed for other reported contiguous iridaborane species.[6–10,15,16]

Of particular interest in this molecule however is the relative positioning of the $IrB_3$ cluster with respect to the formal octahedrally disposed metal-bonding axes, these axes being defined by the approximate dispositions of the ligands in the $Ir(CO)H(PPh_3)_2$ unit. The previously postulated[3] six-fold orthogonal disposition of bonding orbitals about the metal atom together with an eight-electron cluster structure such as (III) would predict that the Ir–P vectors were *trans* to radial *exo*-cluster projections[9,10,17] of the approximate midpoints of the planes Ir(1)B(2)B(3) and Ir(1)B(3)B(4). This, however, is not found. Instead (Figure 3), it can be seen that the Ir(1)P(1)P(2) plane is closely *trans* to the opposing boron atoms B(2) and B(4), and in fact the atoms B(2), B(3), and B(4) together with

**Table 1.** Selected interatomic distances (pm) for $[(CO)(PPh_3)_2HIrB_3H_7]$ with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| (*i*) From the iridium atom | | | |
| Ir(1)–P(1) | 235.7(1) | Ir(1)–P(2) | 236.2(1) |
| Ir(1)–B(2) | 230.3(8) | Ir(1)–B(4) | 229.9(8) |
| Ir(1)–H(1) | 181(8) | Ir(1)–C(1) | 191.0(7) |
| Ir(1)–B(3) | 219.7(8) | | |
| (*ii*) Boron–boron and boron–hydrogen | | | |
| B(2)–B(3) | 183.7(11) | B(3)–B(4) | 182.9(11) |
| B(2)–H(2X) | 114(5) | B(4)–H(4X) | 110(6) |
| B(2)–H(2N) | 93(5) | B(4)–H(4N) | 113(5) |
| B(2)–H(23) | 132(7) | B(4)–H(34) | 131(6) |
| B(3)–H(23) | 132(7) | B(3)–H(34) | 120(6) |
| B(3)–H(3) | 115(5) | | |
| (*iii*) Other | | | |
| P(1)–C(11) | 184.3(3) | P(2)–C(41) | 184.6(3) |
| P(1)–C(21) | 183.7(3) | P(2)–C(51) | 184.2(3) |
| P(1)–C(31) | 184.7(3) | P(2)–C(61) | 183.7(3) |
| C(1)–O(1) | 114.8(8) | | |

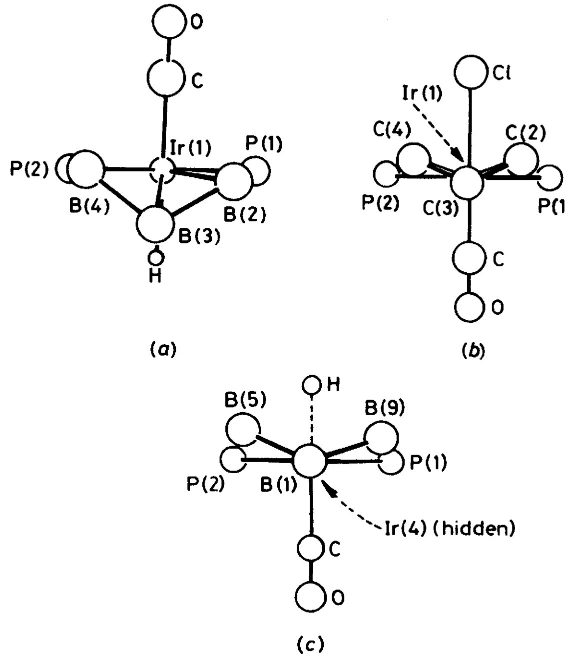


**Figure 3.** ORTEP drawings of the metal and circumjacent atoms, viewed in the IrPP planes of (*a*) $[(CO)(PPh_3)_2HIrB_3H_7]$ (this work), (*b*) the $[(CO)(PMe_2Ph)_2ClIrC_3H_5]^+$ cation (data from ref. 18), and (*c*) $[(CO)(PMe_3)_2HIrB_8H_{11}Cl]$ (data from ref. 9). In the $IrB_3$ cluster (*a*) the Ir–P vectors are thought to be *trans* to two-electron two-centre bonds to B(2) and B(4), whereas in the other two clusters they are thought to be *trans* to three-centre bonds Ir(1)C(2)C(3) and Ir(1)C(3)C(4) [in (*b*)] and Ir(4)B(2)B(9) and Ir(4)B(2)B(5) [in (*c*)]

**Table 2.** Selected angles (°) between interatomic vectors and planes for $[(CO)(PPh_3)_2HIrB_3H_7]$ with estimated standard deviations in parentheses*

(*i*) At the iridium atom

| | | | |
|---|---|---|---|
| P(1)–Ir(1)–P(2) | 107.5(1) | | |
| P(1)–Ir(1)–C(1) | 98.5(2) | P(2)–Ir(1)–C(1) | 94.9(2) |
| P(1)–Ir(1)–H(1) | 83(2) | P(2)–Ir(1)–H(1) | 88(2) |
| P(1)–Ir(1)–B(2) | 82.8(2) | P(2)–Ir(1)–B(4) | 86.6(2) |
| P(1)–Ir(1)–B(3) | 117.7(2) | P(2)–Ir(1)–B(3) | 124.0(2) |
| P(1)–Ir(1)–B(4) | 165.1(2) | P(2)–Ir(1)–B(2) | 169.8(2) |
| B(2)–Ir(1)–B(4) | 83.2(3) | | |
| C(1)–Ir(1)–B(2) | 83.1(3) | C(1)–Ir(1)–B(4) | 84.9(3) |
| C(1)–Ir(1)–B(3) | 108.5(3) | | |
| C(1)–Ir(1)–H(1) | 177(3) | | |
| H(1)–Ir(1)–B(2) | 94(2) | H(1)–Ir(1)–B(4) | 93(2) |
| H(1)–Ir(1)–B(3) | 68(2) | | |

(*ii*) Iridium–boron–boron and boron–boron–boron

| | | | |
|---|---|---|---|
| Ir(1)–B(2)–B(3) | 62.9(3) | Ir(1)–B(4)–B(3) | 63.1(3) |
| Ir(1)–B(3)–B(2) | 69.0(4) | Ir(1)–B(3)–B(4) | 69.0(4) |
| B(2)–B(3)–B(4) | 112.9(6) | | |

(*iii*) Iridium–boron–hydrogen and boron–boron–hydrogen

| | | | |
|---|---|---|---|
| Ir(1)–B(2)–H(2X) | 115(3) | Ir(1)–B(4)–H(4X) | 119(3) |
| Ir(1)–B(2)–H(2N) | 110(3) | Ir(1)–B(4)–H(4N) | 107(3) |
| Ir(1)–B(2)–H(23) | 108(3) | Ir(1)–B(4)–H(34) | 101(3) |
| Ir(1)–B(3)–H(3) | 122(3) | | |
| Ir(1)–B(3)–H(23) | 113(3) | Ir(1)–B(3)–H(34) | 111(3) |
| B(2)–B(3)–H(3) | 124(3) | B(4)–B(3)–H(3) | 122(3) |
| B(2)–B(3)–H(23) | 46(3) | B(4)–B(3)–H(34) | 46(3) |
| B(2)–B(3)–H(34) | 113(3) | B(4)–B(3)–H(23) | 120(3) |
| B(3)–B(2)–H(2X) | 118(3) | B(3)–B(4)–H(4X) | 115(3) |
| B(3)–B(2)–H(2N) | 125(3) | B(3)–B(4)–H(4N) | 125(3) |
| B(3)–B(2)–H(23) | 46(3) | B(3)–B(4)–H(34) | 41(3) |

(*iv*) Hydrogen–boron–hydrogen

| | | | |
|---|---|---|---|
| H(2X)–B(2)–H(2N) | 115(4) | H(4X)–B(4)–H(4N) | 116(4) |
| H(2X)–B(2)–H(23) | 109(4) | H(4X)–B(4)–H(34) | 111(4) |
| H(2N)–B(2)–H(23) | 100(4) | H(4N)–B(4)–H(34) | 101(4) |
| H(3)–B(3)–H(23) | 107(4) | H(3)–B(3)–H(34) | 111(4) |

(*v*) Selected other interatomic angles

| | | | |
|---|---|---|---|
| Ir(1)–P(1)–C(11) | 117.6(1) | Ir(1)–P(2)–C(41) | 114.5(1) |
| Ir(1)–P(1)–C(21) | 120.4(1) | Ir(1)–P(2)–C(51) | 113.8(1) |
| Ir(1)–P(1)–C(31) | 110.1(1) | Ir(1)–P(2)–C(61) | 121.2(1) |
| Ir(1)–C(1)–O(1) | 178.9(6) | | |

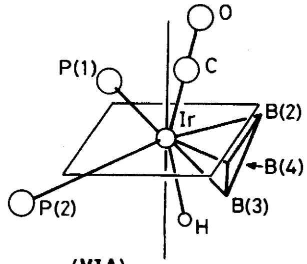
(*vi*) Angles between planes

| | |
|---|---|
| {Ir(1)B(2)B(3)}–{Ir(1)B(3)B(4)} | 126.5 |
| {Ir(1)P(1)P(2)}–{B(2)B(3)B(4)} | 100.6 |

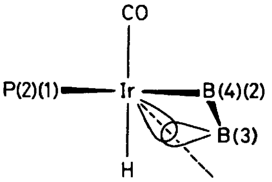
*Here the descriptors X and N refer to *exo-* and *endo-* H atoms respectively.

IrH(1) are all contained *within* the octant of three cartesian axes that may be used to define the octahedral distribution about the metal atom, even allowing for the slight twist of *ca.* 2° which presumably arises from crystal packing forces.

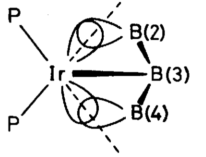
This contrasts with the positionings of the *trihapto* ligands in the metallanonaborane $[(CO)(PMe_3)_2HIrB_8H_{11}Cl]$,[9] and in 'π-allyl' organometallic analogues such as the $[(CO)(PMe_2Ph)_2ClIrC_3H_5]^+$ cation.[18] These are also represented in Figure 3, and are generally thought to have straightforward participation of two bonding orbitals between the metal and the *trihapto* ligand as in **(IV)** (the organometallic compound), or analogous to **(V)** (the metallaborane species); in this latter metallaborane the metal–borane bonding mode has been described in terms of two three-centre (IrBB) bonds with maximum overlap concentrating at tangential face-capping positions *exo* to the IrBB deltahedral faces[9,17] [*cf.* the semi-localized multicentre bond description[19] used in **(III)**].



**(VIA)**



**(VIB)**



**(VIC)**

The metal–borane bonding geometry in the '$IrB_3$' metallatetraborane clearly differs from these, and we would therefore at present interpret the structure on the basis of dominant contributions from a ten-electron cluster as in **(II)** with the involvement of a 'capped octahedral' disposition of seven iridium orbitals as in **(VI)**, with three of these involved in three two-centre bonds to the three boron atoms, with maximum overlap concentrating at tangential edge-bridging positions *exo* to the Ir–B vectors: this is illustrated schematically in **(VIB)** [in which the cluster is viewed in the P(1)P(2)IrB(2)B(4) plane perpendicular to the idealized OCIrH axis] and in **(VIC)** (viewed down the idealized OCIrH axis).

The closer approach (by 10 pm) of the 'capping' B(3) atom to the metal has general precedent in other seven-co-ordinate capped-octahedral 18-electron $d^4$ complexes such as $[MoBr_4(PMe_2Ph)_3]$.[20] In this last species, for example, the capping Mo–Br distance at 242.5 pm is some 13 pm shorter than that for the three flanking bromide groups in 'normal' octahedral positions on the idealized orthogonal axes.

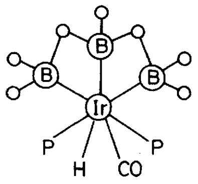
These considerations imply that the effective triborane ligand in the $IrB_3H_7$ cluster species may best be regarded as a tridentate (*i.e.* three electron-pair) *hypho*-$[B_3H_7]^{4-}$ ligand bonding to an [iridium(V)]$^{4+}$ centre as in **(VII)**, rather than as a bidentate (*i.e.* two electron-pair) ligand as previously postulated[3] for this compound, and as largely believed to be the case for hydrocarbon π-allyl ligands exemplified by the iridium(III) species[18] shown in Figure 3(*b*). This is consistent with the increasing recognition that borane ligands have higher electron-attracting powers than isoelectronic hydrocarbon ones of the same formal charge.[14,21,22] In simple terms, the notional removal (following Fehlner)[21] of protons from carbon nuclei in a formal ligand $C_nH_m$, to occupy less shielded bridge-bonding sites in $B_nH_{m+n}$, will result in an increase in total effective nuclear charge experienced by the ligand valence electrons, and thus require an increase in metal valence-shell electron participation in the cluster bonding which is often manifested in increased contributions from higher metal valence states.

In this context it would clearly be of interest to have more definitive structural data on the platinum analogues[1,2] in order to elucidate the $B_3H_7$ ligand behaviour in a 16-electron transition-metal environment, and to distinguish the relative contributions of a platinum(II) eight-electron cluster as in **(I)**, and a platinum(IV) ten-electron cluster as in **(II)**.

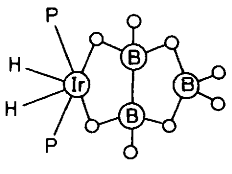
The implied effective valency state of iridium(V) for the metal centre of $[(CO)(PPh_3)_2HIrB_3H_7]$ is of additional interest. It is

**Table 3.** Atomic co-ordinates for $[(CO)(PPh_3)_2HIrB_3H_7]$ with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| *Ir(1)* | 0.123 50(2) | 0.072 46(1) | 0.257 94(2) | C(25) | 0.015 6(2) | 0.337 0(1) | 0.227 1(2) |
| P(1) | −0.020 06(12) | 0.148 90(7) | 0.243 47(11) | C(26) | −0.006 0(2) | 0.279 3(1) | 0.262 4(2) |
| P(2) | 0.288 14(12) | 0.117 72(7) | 0.218 13(11) | C(31) | −0.064 9(2) | 0.155 9(2) | 0.364 2(2) |
| B(2) | −0.017 2(6) | 0.012 7(3) | 0.301 3(6) | C(32) | 0.016 9(2) | 0.177 7(2) | 0.449 4(2) |
| B(3) | 0.064 2(6) | −0.021 2(3) | 0.215 7(6) | C(33) | −0.007 7(2) | 0.176 3(2) | 0.554 9(2) |
| B(4) | 0.222 4(6) | −0.018 6(3) | 0.267 4(6) | C(34) | −0.114 1(2) | 0.153 1(2) | 0.555 2(2) |
| H(1) | 0.060 4(68) | 0.064 9(30) | 0.122 8(60) | C(35) | −0.195 9(2) | 0.131 2(2) | 0.470 0(2) |
| H(2N) | 0.001 2(41) | 0.007 0(23) | 0.371 8(39) | C(36) | −0.171 3(2) | 0.132 6(2) | 0.374 5(2) |
| H(2X) | −0.110 2(43) | 0.028 0(25) | 0.266 8(39) | C(41) | 0.422 0(2) | 0.070 9(2) | 0.251 7(2) |
| H(3) | 0.023 1(46) | −0.034 8(24) | 0.133 0(41) | C(42) | 0.477 9(2) | 0.049 3(2) | 0.179 2(2) |
| H(4N) | 0.267 9(43) | −0.026 1(23) | 0.349 7(39) | C(43) | 0.579 0(2) | 0.014 1(2) | 0.209 5(2) |
| H(4X) | 0.274 3(47) | 0.028 0(24) | 0.212 1(41) | C(44) | 0.624 1(2) | 0.000 6(2) | 0.312 2(2) |
| H(23) | −0.003 4(56) | −0.043 4(30) | 0.271 5(49) | C(45) | 0.568 2(2) | 0.022 2(2) | 0.384 7(2) |
| H(34) | 0.136 3(45) | −0.057 7(28) | 0.257 0(39) | C(46) | 0.467 2(2) | 0.057 4(2) | 0.354 4(2) |
| C(1) | 0.185 9(6) | 0.075 6(2) | 0.401 9(4) | C(51) | 0.270 4(2) | 0.131 5(2) | 0.081 1(2) |
| O(1) | 0.224 1(4) | 0.076 5(2) | 0.488 4(3) | C(52) | 0.305 1(2) | 0.186 0(2) | 0.044 0(2) |
| C(11) | −0.159 0(2) | 0.137 9(2) | 0.147 5(2) | C(53) | 0.300 9(2) | 0.191 9(2) | −0.059 3(2) |
| C(12) | −0.174 8(2) | 0.090 0(2) | 0.077 5(2) | C(54) | 0.262 0(2) | 0.143 3(2) | −0.125 5(2) |
| C(13) | −0.281 2(2) | 0.083 3(2) | 0.005 8(2) | C(55) | 0.227 4(2) | 0.088 8(2) | −0.088 4(2) |
| C(14) | −0.371 8(2) | 0.124 4(2) | 0.004 0(2) | C(56) | 0.231 6(2) | 0.082 9(2) | 0.014 9(2) |
| C(15) | −0.356 0(2) | 0.172 3(2) | 0.074 0(2) | C(61) | 0.351 0(2) | 0.189 1(1) | 0.279 3(2) |
| C(16) | −0.249 6(2) | 0.179 0(2) | 0.145 7(2) | C(62) | 0.286 8(2) | 0.226 7(1) | 0.328 3(2) |
| C(21) | 0.009 2(2) | 0.227 2(1) | 0.207 8(2) | C(63) | 0.332 7(2) | 0.282 7(1) | 0.368 5(2) |
| C(22) | 0.045 8(2) | 0.232 8(1) | 0.118 0(2) | C(64) | 0.442 8(2) | 0.301 0(1) | 0.359 6(2) |
| C(23) | 0.067 4(2) | 0.290 4(1) | 0.082 7(2) | C(65) | 0.507 0(2) | 0.263 3(1) | 0.310 5(2) |
| C(24) | 0.052 3(2) | 0.342 5(1) | 0.137 3(2) | C(66) | 0.461 1(2) | 0.207 4(1) | 0.270 4(2) |



(VII)



(VIII)

also becoming increasingly recognized that the formal iridium(V) valency state is not limited to compounds with highly electronegative ligands, as in the $[IrF_6]^-$ anion,[23] or to polyhydrides such as $[IrH_5(PR_3)_2]$,[24] but that it can occur quite generally in many ostensibly 'softer' bonding environments, such as in the six-vertex organometallic cluster compound $[Ir(\eta^5\text{-}C_5Me_5)Me_4]$, which can be represented as $[1,1,1,1\text{-}Me_4\text{-}\textit{nido}\text{-}1\text{-}IrC_5Me_5]$, [25] and in nine- and ten-vertex metallaborane clusters such as *iso-nido*-$[(PPh_3)(o\text{-}Ph_2PC_6H_4)IrC(OH)B_8H_6(OMe)]$,[6] *iso-closo*-$[(PMe_3)_2HIrB_8H_7Cl]$,[15] and *iso-closo*-$[(PMe_3)_2HIrB_9H_9]$.[8]

In this regard it is of interest to contrast the iridium(V) *arachno* four-vertex 1-metallatetraborane discussed here with the recently described[26] iridium(III) *arachno* four-vertex 2-metallatetraborane species $[(PPh_3)_2H_2IrB_3H_8]$, as represented by the schematic valence-bond structures **(VII)** and **(VIII)** respectively.

Both compounds have similar physical properties, and similar stabilities, and both have a ten-electron cluster bonding scheme, which implies that {iridium(V)} and {iridium(III) + $2H_\mu$} are of very comparable energies in systems such as this. In this connection, the recently reported[27] iridium(III)/iridium(V) effective structure tautomerism in higher metallacarbaborane clusters is of additional relevance, and underlines the conclusion that the valency behaviour of heavy transition-metal centres in these systems is very flexible indeed.[28]

## Experimental

The compound $[(CO)(PPh_3)_2HIrB_3H_7]$ was made as previously described,[3] and crystals suitable for the *X*-ray experiments were grown by solvent diffusion in dichloromethane–pentane.

*Crystal Data.*—$C_{37}H_{38}B_3IrOP_2$, $M = 785.31$, monoclinic, $a = 1\,182.0(3)$, $b = 2\,189.4(4)$, $c = 1\,355.7(3)$ pm, $\beta = 104.27(2)°$, $U = 3.400(1)$ nm$^3$, $Z = 4$, $D_c = 1.534$ g cm$^{-3}$, $F(000) = 1\,560$, space group $P2_1/n$, Mo-$K_\alpha$ radiation, graphite monochromatised, $\lambda = 71.069$ pm, $\mu$(Mo-$K_\alpha$) = 4 031 m$^{-1}$.

*Structure Analysis.*—Cell dimensions were obtained by least-squares treatment of the setting angles of 15 reflections having $35 < 2\theta < 40°$. Intensities of all independent reflections (except the low-order 011 and 020) to $2\theta = 45°$ were measured in the $\omega$–$2\theta$ scan mode, using scan speeds from 1 to 29° min$^{-1}$ according to a pre-scan intensity. The 4 463 intensities were corrected for Lorentz, polarization, and transmission factors, and the 4 119 having $F > 4\sigma(F)$ were used in the structure analysis. Calculations were carried out using the SHELX programs. Full-matrix least-squares refinement with anisotropic temperature factors for Ir and P, isotropic temperature factors for B, C, and O, and with the phenyl groups constrained as regular hexagons with C–C = 139.5 pm, converged at $R = 0.038$. The phenyl hydrogen atoms were then introduced in idealized positions with C–H = 108 pm, and $U_{iso.} = 500$ pm$^2$, giving convergence at $R = 0.035$. A difference map then revealed the eight hydrogens attached to Ir and B, with peak heights of 550—700 e nm$^{-3}$. These were brought into the refinement with both co-ordinates and isotropic temperature factors allowed to refine, giving a final $R$ of 0.032, $R' = 0.043$ (weights based on counting statistics). The atomic co-ordinates and their estimated standard deviations are in Table 3.

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