Reaction of $[Ir(cyclo\text{-}octa\text{-}1,5\text{-}diene)\{P(p\text{-}tolyl)_3\}_2][nido\text{-}7,8\text{-}C_2B_9H_{12}]$ with Hydrogen; Synthesis and *X*-Ray Structure of $3,9\text{-}[(H)_2\{P(p\text{-}tolyl)_3\}_2Ir]\text{-}3,9\text{-}\mu\text{-}(H)_2\text{-}7,8\text{-}C_2B_9H_{10}$

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Summary Treatment of the ion pair, $[Ir(cod)(PR_3)_2]$[*nido*-7,8-$C_2B_9H_{12}$] (cod = cyclo-octa-1,5-diene; R = phenyl, *p*-tolyl) with hydrogen gave *closo*-3,3-$(PR_3)_2$-3-H-3,1,2-$IrC_2B_9H_{11}$ and the novel *nido*-metallocarbaborane, 3,9-[*cis*-$(H)_2$-*trans*-$(PR_3)_2$-Ir]-3,9-μ-$(H)_2$-*nido*-7,8-$C_2B_9H_{10}$.

DURING our continuing investigation of the chemistry of the known alkene hydrogenation and isomerization catalyst, *closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$, we prepared the iridium congener, *closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$IrC_2B_9H_{11}$ (**1a**). Preparation of (**1a**) was conveniently effected by treatment of $[Ir(cod)(PPh_3)_2]$[*nido*-7,8-$C_2B_9H_{12}$] with H_2 (1 atm) in cyclohexane heated to reflux. Characterization of (**1a**) by n.m.r., i.r., and elemental analysis was unequivocal.[1]

When the same reaction was carried out at −22 °C in pentane, a mixture of products was formed. In addition to (**1a**), a pale yellow crystalline complex (**2a**) was found in 40% yield. I.r. and ^1H, ^{31}P, and ^{11}B n.m.r. spectroscopy and microanalysis are consistent with the formulation $(H)_2(PPh_3)_2Ir(C_2B_9H_{12})$. In particular, the ^1H n.m.r. spectrum displays an envelope of broad signals at τ 13—18, assigned to bridging Ir–H–B and B–H–B protons and high field signals at τ 28·0 and 28·5 which are assigned to terminal metal hydrides. In addition, the i.r. spectrum shows absorptions consistent with bridging Ir–H–B groups (ν 1965vw cm^{-1}) and terminal Ir–H groups (ν 2249w cm^{-1}). Since a myriad of linkages between the transition metal and carbaborane cluster is possible, an *X*-ray structure analysis of the related $(H)_2[P(p\text{-}tolyl)_3]_2Ir(C_2B_9H_{12})$ (**2b**) was carried out.

Crystal data: $Ir[P(C_7H_7)_3]_2(H)_2(C_2B_9H_{12})\cdot C_7H_8$, M = 1028·5, triclinic, space group $P\bar{1}$, a = 12·292(4), b = 12·854(3), c = 16·169(4) Å, α = 78·41(1), β = 94·88(1), γ = 102·04(1)°, Z = 2, D_c (119 K) 1·40, D_m 1·32 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ 31·3 cm^{-1}. Data were collected on a Picker FACS-I automated diffractometer at −154 °C. The structure was solved by standard Patterson–Fourier techniques. Full matrix least squares refinements of all atoms† (including the hydrogens bridging the Ir–B bonds) have converged to an agreement factor of 0·044.‡

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† The *p*-tolyl rings were refined as rigid groups. After the location and refinement of all atoms except the four hydrogens bound to the Ir atom and the two partially occupied carbaborane hydrogens a difference-Fourier synthesis was calculated. The two tallest peaks in the map were attributed to the bridging hydrogen atoms. Their final refined positions are less than two standard deviations away from their Fourier map positions. The only other significant peak in the map in the vicinity of the Ir atom was in the proper position for a terminal hydride atom. Since the second hydride atom was not located (even in maps of decreasing $\sin\theta/\tau$ cutoff) this atom was not included in the final cycles of refinement. The successful refinement of these bridging hydrogen atoms is due at least in part to their distance from the metal atom.

‡ The crystal used for data collection was approximately equidimensional (0·10 mm × 0·12 mm × 0·14 mm). An analytical absorption correction was made; the minimum and maximum absorption coefficients were 0·7462 and 0·8407, respectively. Structure factors were weighted by $1/\sigma^2$ where σ is the standard deviation of F. In the final cycle of least squares no shift was larger than one-tenth of its corresponding estimated standard deviation. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The molecule is illustrated in the Figure, with selected bond distances and angles. The crystal structure formally consists of a discrete *cis*-$[(H)_2\{P(p\text{-tolyl})_3\}_2Ir]^+$ fragment bonded to two terminal B–H bonds of a $[C_2B_9H_{12}]^-$ anion.

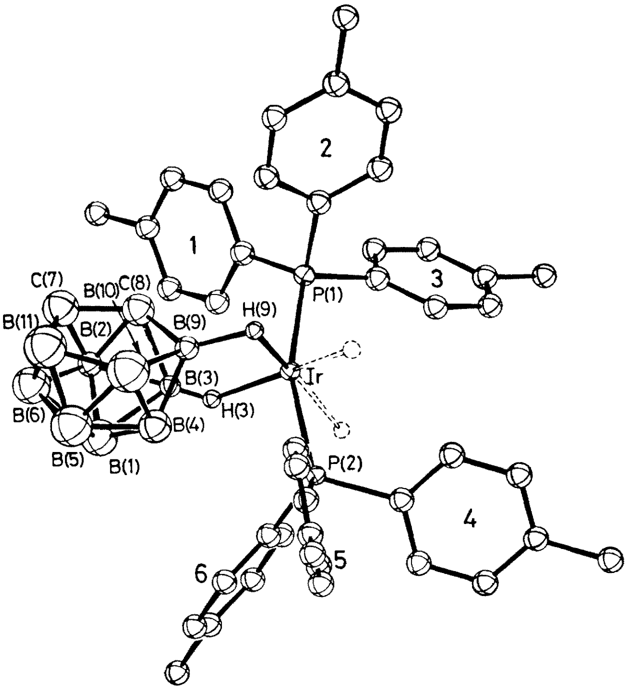


FIGURE. The molecular structure of 3,9-$[(H)_2\{P(p\text{-tolyl})_3\}_2Ir]$-**3**,9-$\mu$-$(H)_2$-7,8-$C_2B_9H_{10}$. Some important bond lengths are: Ir–P(1), 2·312(3); Ir–P(2), 2·301(3); Ir–H(3), 1·85(7); Ir–H(9), 2·02(10); Ir–B(3), 2·480(11); Ir–B(9), 2·452(11); B(3)–H(3) 1·4(1); B(9)–H(9), 1·3(1) Å; bond angles: P(1)–Ir–P(2), 158·9(1); P(1)–Ir–H(3), 102(2); P(1)–Ir–H(9), 94(3); P(2)–Ir–H(3), 94(2); P(2)–Ir–H(9), 95(3); H(3)–Ir–H(9), 104(4); B(3)–Ir–B(9), 40·8(4), Ir–H(3)–B(3), 98(4); Ir–H(9)–B(9), 94(6)°.

The crystal displays an unusual disorder featuring the carbaborane cluster. Packing within the crystal is apparently determined by the tri-*p*-tolylphosphine ligands, leaving the carbaborane cluster free to adopt 1 of 2 different orientations in a 60:40 ratio. Each orientation of the carbaborane cluster, however, is constrained so that the Ir atom is bound to the same two B–H bonds; additionally the carbon atom positions within the carbaborane are also constrained to be identical in the two orientations. Consequently, the two species present in the crystal are chemically equivalent.

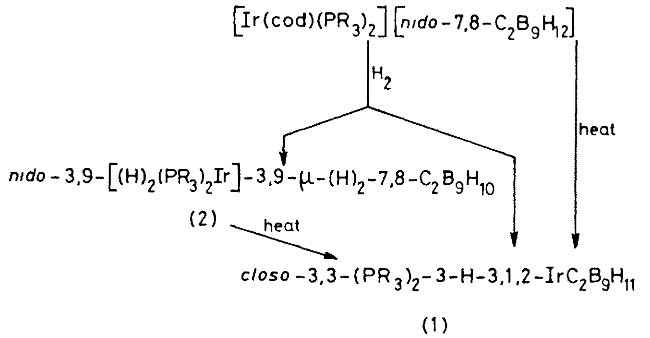
An especially noteworthy feature of the complex is the mode of interaction of the $[(H)_2L_2Ir]^+$ fragment with the $[C_2B_9H_{12}]^-$ group. The iridium atom interacts with the B(3)–H(3) and B(9)–H(9) bonds thereby completing the octahedral co-ordination about the metal atom. Exopolyhedral bonding of a transition metal to a borane cluster has been previously observed in $[(Ph_3P)_2Cu]_2B_{10}H_{10}\cdot CHCl_3$,[2] [Cu–H 1·97(6), Cu–B 2·30(1) Å].

Comparison of the Ir–B and Ir–H distances in (**2b**) with those in $Ir(B_5H_8)(CO)(PPh_3)_2$ [Ir–B (H bridged) 2·250(6), Ir–H 1·73 Å],[3] a *nido*-pentagonal pyramid metalloborane, indicates a weaker Ir–carbaborane interaction in (**2b**) [Ir–B 2·46(1), Ir–H 1·94(8) Å]. Note that this Ir–H bond length is also longer than the Ir–H bridging bond lengths found in the recently reported $[(C_5Me_5)_2Ir_2(\mu\text{-}H)_3]BF_4$ [Ir–H 1·75(1) Å, neutron diffraction].[4]

Although the terminal Ir–H hydride ligands of (**2b**) were not located in the structure analysis the geometry about the Ir atom is clearly that of a distorted octahedron with the symmetric hydrides occupying the two *cis* 'vacant' positions.

Three centre M–H–B (M = transition metal) bonding of exopolyhedral B–H units is seen in a variety of metallocarbaborane complexes.[5] However, all of these systems involve *closo* carbaboranyl or metallocarbaboranyl units. Previous to this work, the only M–H–B bonding of exopolyhedral B–H units of a *nido* carbaboranyl unit were found in the main group compounds; 7,8-μ-dialkylaluminio-1,2-dicarba-*nido*-undecaborane(13) (alkyl = Me, Et) and its gallium analogues[6,7]§ in which the M–H–B bonds can be viewed as formally donating two electrons each to the aluminium or gallium to satisfy its 'octet.' The same formalism allows (**2a**) to be seen as a stable eighteen electron organometallic compound.

When the *nido* compounds (**2a**) or (**2b**) were heated in benzene, the thermodynamically favoured *closo* compound (**1a**) and its tri-*p*-tolylphosphine analogue (**1b**) were obtained (both in 90% yield) (Scheme). This behaviour is analogous to that of the aluminium and gallium *nido*-carbaborane systems.[6]



SCHEME. **a**; R = Ph
b; R = *p*-tolyl
cod = cyclo-octa-1,5-diene

As previously noted, heating $[Ir(cod)(PPh_3)_2]$[*nido*-7,8-$C_2B_9H_{12}$] in cyclohexane in the presence of hydrogen gave primarily the *closo* compound (**1a**). However, trace amounts of the *nido* compound (**2a**) were also isolated under these reaction conditions. When the $[Ir(cod)(PR_3)_2]$[*nido*-7,8-$C_2B_9H_{12}$] (R = phenyl and *p*-tolyl) compounds were heated in cyclohexane without hydrogen, only the *closo* compounds (**1a**) and (**1b**) were obtained, with no trace of the *nido* compounds.

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§ The cage numbering system in this paper is consistent with that favoured by I.U.P.A.C. for *nido* carbaboranes, and is different from the numbering scheme in ref. 4.

We thank the National Science Foundation and the Office of Naval Research for partial support. We also thank the National Science Foundation for the purchase of the Picker Diffractometer.

(*Received*, 31*st July* 1979; *Com.* 832.)

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