A Fluxional *arachno*-1-Metallapentaborane, [1,1,1-(CO)$(PMe_3)_2$(1-IrB_4H_9)]

By **Jonathan Bould, Norman N. Greenwood,*** and **John D. Kennedy**, Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT

The reaction of *nido*-$B_9H_{12}^-$ with *trans*-[Ir(CO)Cl$(PMe_3)_2$] yields several new compounds, among which is the pale yellow *arachno*-1-metallapentaborane [1,1,1-(CO)$(PMe_3)_2$(1-IrB_4H_9)]. This compound bears the same relation to *arachno*-B_5H_{11} as *nido*-[1,1,1-$(CO)_3$(1-FeB_4H_8)] bears to *nido*-B_5H_9. The fluxionality of the compound and its ^1H, ^{11}B, and ^{31}P n.m.r. spectra are described.

ALTHOUGH a number of *nido*-5-vertex metallapentaboranes are known,[1-4] there appear to be no well characterized examples of analogous *arachno*-5-vertex species. Here we report the *arachno*-1-metallapentaborane [1,1,1-(CO)$(PMe_3)_2$(1-IrB_4H_9)], which is structurally an analogue of *arachno*-pentaborane, B_5H_{11}.

The compound was isolated as a very pale yellow, air stable, diamagnetic solid in low yield (*ca.* 1%) from the products of the reaction of the *nido*-$B_9H_{12}^-$ anion with *trans*-[Ir(CO)Cl$(PMe_3)_2$]. Quantities were insufficient for conventional elemental analysis but low-temperature n.m.r. spectroscopy (Table) shows that the molecule contains two inequivalent PMe_3 ligands, four distinct boron atoms, and nine borane hydrogen atoms, but no terminal or bridging Ir–H atoms. In addition there is a terminal iridium-carbonyl group [ν(C=O) at 1 990 cm^{-1}] and so the compound is reasonably formulated as [Ir(B_4H_9)(CO)$(PMe_3)_2$]. In accord with this the 54-eV † low-resolution mass spectrum indicated a high-mass molecular ion ' cut-off ' peak at $m/e = 426$ ($^{193}Ir^{31}P_2{}^{16}O^{12}C_7{}^{11}B_4{}^1H_{27}$ requires $m/e = 426.14$); principal initial fragmentations included loss of CO and loss of H atoms from the molecular ion as expected.

The low-field (' high-frequency ') pair of ^{11}B n.m.r. resonances are each associated with one terminal-proton resonance, and the high-field (' low-frequency ') pair are each associated with two terminal-proton resonances. These properties together with those of the bridging hydrogen resonances and the overall shielding behaviour largely parallel those (Table) of the basal atoms in *arachno*-B_5H_{11} (1) which leads to the structure (2) for the metallaborane cluster in the iridium complex. It will be noted that *arachno*-[Ir(B_4H_9)(CO)$(PMe_3)_2$] has two more skeletal valence electrons than the known *nido*-[Fe(B_4H_8)$(CO)_3$],[1] consistent with Wade's electron-counting rules.

The similarity of the n.m.r. behaviour of B_5H_{11} and [Ir(B_4H_9)(CO)$(PMe_3)_2$] further indicates that the apex-to-basal bonding in both compounds is very similar. The metallaborane may therefore be regarded as an 18-electron iridium(III) species with a quasi-octahedral geometry as in structure (3). Two of the three metal–borane co-ordination sites are taken up by two Ir–B–B three-centre bonds [valence-bond structures (3a) and (3b)] and the third by the (formal) lone pair which may be considered as contributing two electrons to the cluster electron count in the same way as the apical *endo*-terminal two-electron bond to hydrogen in B_5H_{11} [structure (4)]. It must be emphasized that other contributory canonical forms may be written down for structures (3a), (3b), and (4); for example in (3a) and

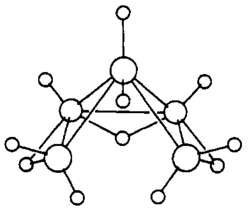
N.m.r. data for *arachno*-[1,1,1-(CO)$(PMe_3)_2$(1-IrB_4H_9)] [a] and *arachno*-B_5H_{11} [b]

Assignment	$\delta(^{11}B)$/p.p.m.[c,e] 128 MHz, 19 °C	$\delta(^1H)$/p.p.m.[d,e,f] 100 MHz, −53 °C	$\delta(^{11}B)$/p.p.m.[c,e] 32 MHz, 55 °C	$\delta(^1H)$/p.p.m.[d,e] 100 MHz, 42 °C	$\delta(^{11}B)$/p.p.m.[c] B_5H_{11}	$\delta(^1H)$/p.p.m.[d] B_5H_{11}
2 or 5	−16.0 [g]	+1.79 +0.86	−15.2	+2.09	+7.44 [h]	+3.5 [i]
2 or 5	−14.3 [g]	+2.09 +0.79		+0.99		+3.1 [j]
3 or 4	+0.8 [k]	+3.05	+2.3	+3.10	+0.47 [l]	+3.4
3 or 4	+3.9 [k]	+2.89				
Bridge		−4.50 −4.82		−4.63		−0.6
		−3.54		−3.55		−2.0

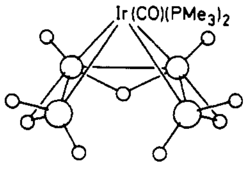
[a] Dilute solution in $CDCl_3$. [b] Neat liquid containing $SiMe_4$; J. B. Leach, T. Onak, J. Spielman, R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, 1970, **9**, 2170. [c] $\delta(^{11}B)$ to low-field (high-frequency) of $BF_3{\cdot}OEt_2$. [d] $\delta(^1H)$ to low-field (high-frequency) of $SiMe_4$. [e] Correspondence between individual ^{11}B and ^1H resonances established by selective ^1H-{^{11}B} spectroscopy. [f] Also at −53 °C, $\delta(^1H)(PMe_3) = +1.69$ and $+1.52$ p.p.m., $^2J(^{31}P–^1H) = 9.5 \pm 0.5$ Hz in each case; $\delta(^{31}P) = -52.6$ p.p.m. ($w_{\frac{1}{2}}$ *ca.* 8 Hz) and −59.4 p.p.m. ($w_{\frac{1}{2}}$ *ca.* 20 Hz), $^2J(^{31}P–^{31}P) = 7 \pm 1$ Hz; $\delta(^{31}P)$ to low-field (' high-frequency ') of $\delta(^{31}P)$ (85% H_3PO_4) = zero. [g] Approx 1 : 2 : 1 triplet, $^1J(^{11}B–^1H)$ (mean) *ca.* 135 Hz. [h] Approximate 1 : 2 : 1 triplet, $^1J(^{11}B–^1H)$ (mean) *ca.* 132 Hz. [i] $^1J(^{11}B–^1H) = 127$ Hz. [j] $^1J(^{11}B–^1H) = 135$ Hz. [k] Doublet, $^1J(^{11}B–^1H)$ *ca.* 160 Hz. [l] $^1J(^{11}B–^1H) = 160$ Hz.

---

† Throughout this note: 1 eV = 1.602 18 × 10^{-19} J.

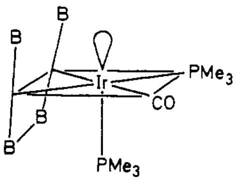


(1)

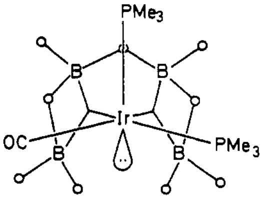


(2)

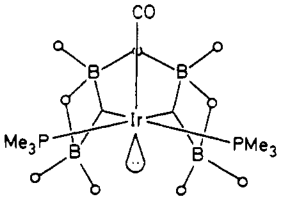
(3b) there will be substantial Ir–B(2)–B(5) bonding *via* the formal lone pair. The IrL_2L' unit (where L,L′ are two-electron donor ligands) is in this instance isoelectronic in Wade's terms with the BH_2 unit of B_5H_{11}. Alternatively the compound may be regarded formally as a complex between the hypothetical $B_4H_9^{3-}$ ligand and $[Ir(CO)(PMe_3)_2]^{3+}$. As indicated by the n.m.r. evidence, an asymmetric distribution of the PMe_3 and CO ligands [*e.g.* structure (3a)] is preferred over a symmetrical one [*e.g.* structure (3b)], possibly for steric reasons.



(3)

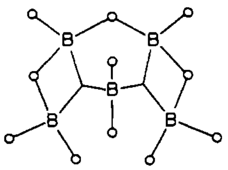


(3a)

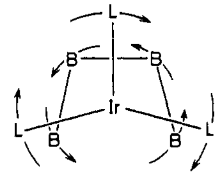


(3b)

At higher temperatures the molecule is fluxional; the two PMe_3 groups become equivalent on a time average, and the basal borane ^{11}B and ^{1}H nuclei (with the exception of the unique bridging proton) become equivalent in pairs (Table) implying a rapid mutual pseudorotation [5,6] of the η^4-borane and the $(PMe_3)_2(CO)$ groupings as in (5). The apparent 'transition temperature' depends upon the frequency separation of the n.m.r. features monitored to examine the transition from static to fluxional behaviour. This was conveniently done using the two singlet PMe_3 resonances in the 100-MHz ^{1}H-{^{31}P(broad-band noise)} n.m.r. spectrum. These are separated by 16.5 Hz at lower temperatures and coalesced at 17.5 °C, implying an activation energy $\Delta G^{\ddagger}$ of *ca.* 63 kJ mol^{-1} at 17.5 °C for the pseudorotation. Similarly, in the 32-MHz ^{11}B-{^{1}H(broad-band noise)} spectrum the $^{11}B(3)$ and $^{11}B(4)$ resonances (low-temperature separation 135 Hz) coalesced at 46 °C, implying that $\Delta G^{\ddagger}$ is also *ca.* 63 kJ mol^{-1} at 46 °C. This is of a similar order of magnitude to that for butadiene ligand pseudorotation in compounds such as $[Fe(CH_2CHCHCH_2)(CO)_3]$,[7] but somewhat lower than that observed for the other known example of η^4-borane ligand pseudorotation, in $[7,7\text{-}(PMe_2Ph)_2\text{-}nido\text{-}7\text{-}PtB_{10}H_{12}]$.[5,6]



(4)



(5)

Since the product occurs in only very low yield in our reaction, comment on the mechanism of formation would be too speculative at this stage, although it is of interest to note that the same compound is also present in low yield in the product mixture from the reaction of the *nido*-$B_6H_9^-$ anion with $[Ir(CO)Cl(PMe_3)_2]$.[8] A more ready and stoicheiometric synthesis might perhaps derive from the reaction of the *arachno*-$B_4H_9^-$ anion with $[Ir(CO)Cl(PMe_3)_2]$, but this is outside our current area of interest.*

EXPERIMENTAL

The initial reaction was carried out under an atmosphere of dry nitrogen although subsequent manipulations were generally carried out in air. The compounds $[NEt_4][B_9H_{12}]$ and $[Ir(CO)Cl(PMe_3)_2]$ were made essentially according to the literature.[9,10] Proton (100-MHz), 40-MHz ^{31}P, and 32-MHz ^{11}B n.m.r. spectroscopy were carried out on a JEOL FX 100 instrument; heteronuclear decoupling techniques have been adequately described elsewhere.[6,11] Boron-11 (128-MHz) spectra were recorded on a Bruker WH 400 instrument at the University of Sheffield. Mass spectroscopy was performed on an A.E.I. MS 30 double-beam instrument.

The compound $[1,1,1\text{-}(CO)(PMe_3)_2\text{-}arachno\text{-}1\text{-}IrB_4H_9]$ was isolated as follows: $[Ir(CO)Cl(PMe_3)_2]$ (0.70 g, 0.17 mmol) was added to a solution of $[NEt_4][B_9H_{12}]$ (0.83 g, 0.34 mmol) in CH_2Cl_2 (10 cm^3). The solution was stirred for 10 min, then reduced in volume (*ca.* 2 cm^3), and applied to a preparative thin-layer chromatographic plate [Kieselgel 60 G (Merck), *ca.* 20 × 20 × 0.1 cm^3]. The plate was developed using CH_2Cl_2–pentane (30 : 70) as eluting medium. The yellow band at R_f 0.35 was removed and extracted, then rechromatographed until pure; yield 9 mg, *ca.* 1%.

We thank the S.E.R.C. for support, and Dr. R. Greatrex for very helpful co-operation with mass spectrometry.

[1/1102 *Received*, 13*th July*, 1981]

---

* *Note added at proof:* Such a route has been used successfully to synthesize $[1,1,1\text{-}(CO)(PMe_2Ph)_2(1\text{-}IrB_4H_9)]$ in 60% yield (S. K. Boocock, M. J. Toft, and S. G. Shore, 182nd Amer. Chem. Soc. National Meeting, New York, 23—28th August, 1981, Abstract INOR 149.

REFERENCES

[1] N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 1974, 718.

[2] V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, 1973, **95**, 5078.

[3] V. R. Miller, R. Weiss, and R. N. Grimes, *J. Am. Chem. Soc.*, 1977, **99**, 5646.

[4] L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 1976, 118.

[5] S. K. Boocock, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1980, 305.

[6] S. K. Boocock, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1981, 2573.

[7] L. Kruczynski and J. Takats, *J. Am. Chem. Soc.*, 1974, **96**, 932.

[8] Unpublished work by the present authors in collaboration with R. Greatrex and G. Jump.

[9] B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1961, **83**, 2669.

[10] R. T. Markham, E. A. Dietz, and D. R. Martin, *Inorg. Synth.*, 1978/9, **18**, 153.

[11] S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.