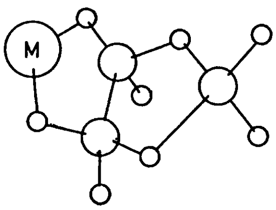
Reactions of the Octahydrotriborate(1−) Anion, $[B_3H_8]^-$, with Some Complexes of Cobalt(I), Cobalt(II), Rhodium(I), and Iridium(I), and the Characterization of the ' Borallyl ' Complex $[Ir^{III}(\eta^3\text{-}B_3H_7)(CO)H(PPh_3)_2]$

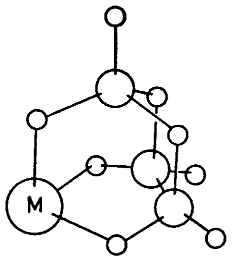
By **Norman N. Greenwood,* John D. Kennedy,** and **David Reed,** Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT

The octahydrotriborate(1−) anion, $[B_3H_8]^-$, reacts with amine and tertiary phosphine complexes of cobalt(I) and cobalt(II) halides to give *arachno*-triborane-ligand adducts, B_3H_7L, together with $B_2H_4L_2$ and BH_3L (where L = pyridine or tertiary phosphine). A similar reaction occurs with *trans*-$[Rh^I(CO)Cl(PPh_3)_2]$ and with $[Ir^I(CO)Cl(PPh_3)_2]$. The latter complex also yields the novel ' borallyl ' compound $[Ir^{III}(\eta^3\text{-}B_3H_7)(CO)H(PPh_3)_2]$ which may also be described as a *nido*-iridatetraborane, $[(IrB_3H_7)(CO)H(PPh_3)_2]$. The spectroscopic properties and structure of this compound are discussed. The $[B_3H_8]^-$ ion does not react with $[Ir^I(CO)(dppe)_2]^+$ but $[Ir^I(dppe)_2]^+$ is converted into $[Ir^{III}H_2(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$).

THE octahydrotriborate(1—) anion, $[B_3H_8]^-$, is known to act either as a bidentate [1,2] or a tridentate [2,3] ligand towards a number of metals [structures (I) and (II)] and we sought to determine whether other structural types could be obtained by treating $[B_3H_8]^-$ with suitable complexes of other metals. The choice of cobalt, rhodium, and iridium as metal centres was made in the knowledge that cobalt complexes produce a fascinating variety of metalloboranes when allowed to react with pentaborane species under appropriate conditions; [4] iridium complexes also exhibit some interesting chemistry with *nido*-pentaboranyl derivatives,[5,6] including insertion and cluster expansion to an iridahexaborane.[6] Following some preliminary work in this laboratory by Ian Ward,[7] we now report the results obtained by the reaction of $[B_3H_8]^-$ with selected pyridine (py) and tertiary phosphine complexes of cobalt-(I) and -(II), rhodium(I), and iridium(I).



(I)



(II)

RESULTS AND DISCUSSION

The reaction of $[CoBr(PPh_3)_3]$, $[CoCl_2(PPh_3)_2]$, $[CoCl_2(PMePh_2)_2]$, and $[CoCl_2(py)_2]$ with either $Tl[B_3H_8]$ or $[NMe_4][B_3H_8]$ at room temperature yielded the *arachno*-triborane-ligand adducts, B_3H_7L, where L was triphenylphosphine, methyldiphenylphosphine, or pyridine, as appropriate. In addition, varying amounts of $B_2H_4L_2$ and BH_3L were formed, but these are known to be decomposition and/or cleavage products of B_3H_7L, especially in the presence of an excess of ligand.[8,9] In none of these reactions was there any indication of the formation of cobalt-containing borane species.

The initial reaction to form the ligand adducts B_3H_7L probably results from a one-electron redox process involving the metal centre [equation (1)] which may occur *via* an initial metal–triborane complex. In this context

$$[B_3H_8]^- + Co^{n+} \longrightarrow Co^{(n-1)+} + \tfrac{1}{2}H_2 + \{B_3H_7\} \xrightarrow{L} B_3H_7L \quad (1)$$

it is known that one-electron electrolytic oxidation of $[B_3H_8]^-$ in the presence of ligands yields the adducts B_3H_7L,[10,11] and that Hg^{II} is also reduced in similar reactions to form B_3H_7L.[12] We have likewise found that one-electron oxidation by halogen [reaction (2)]

$$[B_3H_8]^- + \tfrac{1}{2}I_2 + L \longrightarrow I^- + \tfrac{1}{2}H_2 + B_3H_7L \quad (2)$$

produces the same result, although the synthetic utility of this reaction is limited in practice by the formation of the monoborane adduct BH_3L as a major by-product. We may also mention parenthetically that in other work [13] we have found that, when appropriate, a better synthetic route to B_3H_7L is *via* the ligand hydrohalide, as in reaction (3). In this reaction the principal by-product is

$$[B_3H_8]^- + [Hpy]I \longrightarrow I^- + H_2 + B_3H_7(py) \quad (3)$$

the salt $[BH_2(py)_2]I$ which is more easily separable. Both reactions (2) and (3) have parallels in the chemistry of the tetrahydroborate anion, $[BH_4]^-$.[14,15]

The reactions of $Tl[B_3H_8]$ with *trans*-$[Rh^I(CO)Cl(PPh_3)_2]$ and with *trans*-$[Ir^I(CO)Cl(PPh_3)_2]$ also gave phosphine-boranes but, in addition, the iridium complex gave a metalloborane which can be formulated as the ' μ-borallyl ' hydroiridium(III) complex $[Ir^{III}(\eta^3\text{-}B_3H_7)(CO)H(PPh_3)_2]$ rather than the initially expected hydrogen bridge-bonded iridium(I) octahydroborate complex which has the same empirical formula, $[Ir^I(B_3H_8)(CO)(PPh_3)_2]$ [reaction (4)]. The alternative formulation of

$$[B_3H_8]^- + [Ir^I(CO)Cl(PPh_3)_2] \longrightarrow Cl^- + [Ir^{III}(\eta^3\text{-}B_3H_7)(CO)H(PPh_3)_2] \quad (4)$$

this compound as an iridatetraborane derivative, $[(IrB_3H_7)(CO)H(PPh_3)_2]$, is entirely equivalent but is probably to be preferred since it emphasizes the presence of an IrB_3 cluster and the absence of M–H–B bonds such as are found in the normal η^2 and η^3 complexes of $[B_3H_8]^-$ shown in structures (I) and (II). Thus, the ^{11}B n.m.r.

Hydrogen-1 and ^{11}B n.m.r. data for $[(IrB_3H_7)(CO)H(PPh_3)_2]$ in CD_2Cl_2 solutions at 23 °C

Position [a]	$\delta(^{11}B)$/p.p.m.[b]	$\delta(^{1}H)$/p.p.m.[b]
1	(Ir atom)	-11.52 [c]
3	$+3 \pm 2$ ($w_{\frac{1}{2}}$ *ca.* 350 Hz)	$+3.26$ (H_d) [a]
2, 4	-15 ± 2 ($w_{\frac{1}{2}}$ *ca.* 500 Hz)	$+1.74$ $+1.45$ [d]
H_μ		-5.01 (H_c) [a]

[a] Numbering as in structures (IV). [b] To high frequency of $OEt_2 \cdot BF_3$ (for ^{11}B) and $SiMe_4$ (for ^{1}H). [c] Triplet, $^2J(^{31}P-Ir-^{1}H) = 15.7$ Hz. [d] H_a and H_b [structure (IV)] have different environments.

spectrum (Table) showed two broad resonances ($w_{\frac{1}{2}}$ 500 and 350 Hz respectively at 25 °C in CH_2Cl_2) of relative area 2 : 1 at $\delta(^{11}B)$ -15 and $+3$ p.p.m. respectively. These values differ markedly from those for known transition-metal $[B_3H_8]^-$ complexes which have resonances within the ranges $\delta(^{11}B)$ -41 ± 3 (relative area 2) and -1 ± 6 p.p.m. (relative area 1).[1,2,16] The ^{1}H n.m.r. spectrum (CD_2Cl_2 solution) also differed from that expected for a straightforward $[B_3H_8]^-$ derivative (see Table). The high-field resonance (relative area 1) at $\delta(^{1}H)$ -11.6 p.p.m. had a 1 : 2 : 1 triplet structure which was shown by $^{1}H-\{^{31}P\}$ experiments to be due to coupling $^2J(^{31}P-Ir-^{1}H)$ 15.7 Hz and is thus reasonably assigned to a terminal Ir–H proton. At 25 °C the remainder of the boron hydride resonances were broad and occurred at $\delta(^{1}H)$ -5.01 and *ca.* $+1.7$ p.p.m. with relative areas 2: *ca.* 5 respectively. On cooling to $\leqslant$ *ca.* -50 °C the larger resonance (area 5) became resolved into three peaks (so-called ' thermal decoupling ')[17] at $+3.26$, $+1.74$, and $+1.45$ p.p.m., with relative areas 1 : 2 : 2 respectively, of which the larger two were marginally sharpened but otherwise unchanged in $^{1}H-\{^{31}P\}$ decoupling experiments (Figure 1). This 1 : 2 : 2 structure was also observed at room temperature under conditions of complete ^{11}B decoupling; in this case selective $^{1}H-\{^{11}B\}$ experiments showed that the protons at $\delta(^{1}H)$ $+1.74$ and $+1.45$ were associated with the boron resonance at $\delta(^{11}B)$ -15 p.p.m., and that those at $\delta(^{1}H)$ $+3.26$ p.p.m. were associated with the boron resonance at $\delta(^{11}B)$ $+3$ p.p.m. The resonance (area 2) at $\delta(^{1}H)$ -5.01 p.p.m. did not show differential sharpening and may be ascribed to B–H–B bridging protons. This ^{1}H spectrum is similar to those reported for the only other known ' borallyl ' complexes, the platinum(II) species $[(Pt^{II}B_3H_7)(PR_3)_2]$,[18,19] which also have a 1 : 2 : 2 : 2 pattern for the borane protons, and contrasts with those of metal–$[B_3H_8]^-$ complexes,[1,2,16] which have a 1 : 1 : 2 : 2 : 2 pattern.

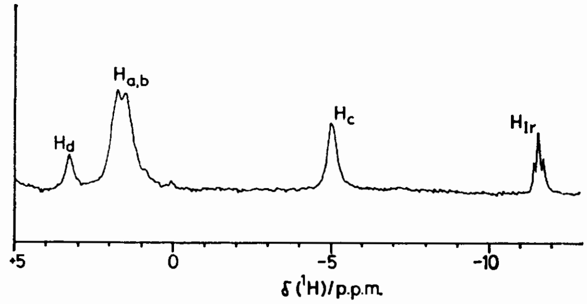
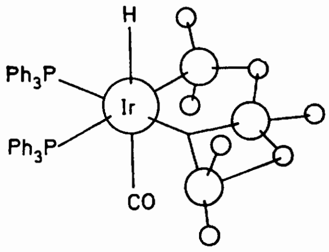


FIGURE 1 100-MHz $^{1}H-\{^{11}B$(broad band)$\}$ spectrum of the borane protons of $[(IrB_3H_7)(CO)H(PPh_3)_2]$ in CD_2Cl_2 solution at -40 °C. The ^{1}H labelling is as in structure (IVA)

The ^{1}H and ^{11}B data imply a structure such as (III) with an octahedrally co-ordinated metal atom bonded to the η^3-B_3H_7 ligand *via* one two-electron two-centre Ir–B bond and one two-electron three-centre IrB_2 bond. The i.r. spectrum (Figure 2) is also consistent with this. A localized bonding structure, however, makes the two phosphine ligands inequivalent whereas the ^{31}P n.m.r. spectrum shows only one resonance at $\delta(^{31}P)$ $+6.4$ p.p.m.; this implies either a resonance hybrid (IVA), or rapid equilibration in solution (IVB, IVC).



(III)

A similar conclusion derives from the ^{1}H and $^{1}H-\{^{11}B\}$ n.m.r. spectra (Figure 1 and Table) which show only one resonance each for the proton types H_a, H_b, H_c, and H_d. By contrast, the ^{1}H n.m.r. spectrum of $[Pt(B_3H_7)(PMe_2Ph)_2]$ was interpreted to suggest that the solid-state delocalized structure, as determined by *X*-ray structure analysis, and which is equivalent to (IVB) or (IVC), also persisted in solution.[19]

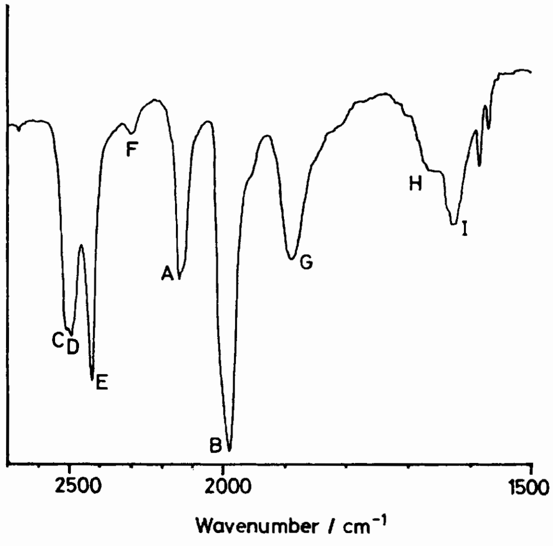
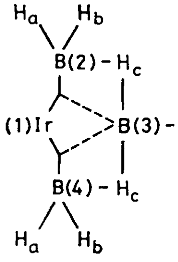
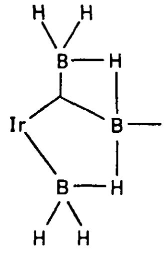


FIGURE 2 Infrared spectrum (1 500—2 700 cm^{-1}) of $[(IrB_3H_7)(CO)H(PPh_3)_2]$ (KCl disc) showing absorptions due to: (A), ν(Ir–H); (B), ν(CO); and (C)—(H), the $[B_3H_7]^{2-}$ ligand. The spectrum excluding (A) and (B) is very similar to that reported[19] for $[(PtB_3H_7)(PMe_2Ph)_2]$. Note the change of scale at 2 000 cm^{-1}

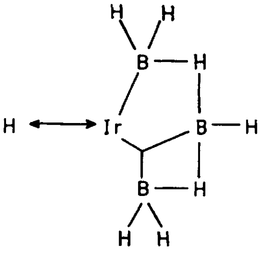
The structure of the iridium complex can be regarded as that of an *arachno*-$[B_3H_7]^{2-}$ ligand co-ordinated to the metal centre of $[Ir(CO)H(PPh_3)_2]^{2+}$; the iridium thus adds an additional apex but no further bonding electrons to the cluster thereby converting the *arachno*-triborane anion into a *nido*-four-vertex cluster. Calculations[20] indicate that the most stable topology for the unstable parent *nido*-tetraborane species B_4H_8 is the 'vacant-orbital' configuration (2112) as in structure (VA) and that the most stable geometry for this species would be the 'butterfly' conformation shown in (VB). (Note that this numbering differs from that in ref. 20.) The 'borallyl' metal complexes can then be considered to be formally derived from this structure by replacement of the neutral BH group at position 1 with a neutral $Ir(CO)H(PPh_3)_2$ or $Pt(PR_3)_2$ group since all these moieties would contribute two electrons to the deltahedral cluster. The compounds can therefore be described as metalla-*nido*-tetraboranes and written as $[(IrB_3H_7)(CO)H(PPh_3)_2]$ and $[(PtB_3H_7)(PR_3)_2]$.



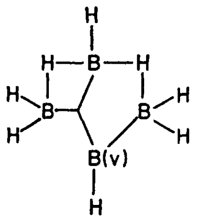
(IVA)



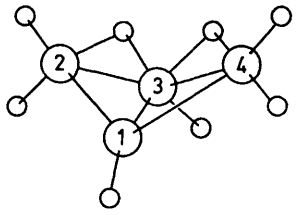
(IVB)



(IVC)



(VA)



(VB)

The mechanism of formation of this iridium(III)-triborane species from the iridium(I) halide complex and $[B_3H_8]^-$ is of particular interest, and resembles in many respects the recently reported[6] oxidative insertion of iridium(I) into a *nido*-pentaboranyl cluster to produce an iridium(III) irida-*nido*-hexaborane. This has further synthetic implications which are currently under investigation.

Finally it is convenient to report here that the reaction of $[B_3H_8]^-$ with the co-ordinatively more saturated and less flexible species $[Ir^{I}(CO)(dppe)_2]Cl$ (where dppe is $Ph_2PCH_2CH_2PPh_2$) merely produced the ionic salt $[Ir^{I}(CO)(dppe)_2][B_3H_8]$. By contrast $[Ir^{I}(dppe)_2]^+$ was hydrogenated to produce $[Ir^{III}H_2(dppe)_2]^+$ under similar conditions; this behaviour is however similar to that which occurs with a number of *nido*-decaboranyl derivatives which have been discussed elsewhere.[21]

EXPERIMENTAL

General.—Reactions were carried out under nitrogen or *in vacuo*. The compounds $[Rh(CO)Cl(PPh_3)_2]$ and $[NMe_4][B_3H_8]$ were obtained commercially and $[CoBr(PPh_3)_3]$, $[CoCl_2(PPh_3)_2]$,[22,23] $[CoCl_2(NC_5H_5)_2]$,[24] $[Ir(CO)Cl(PPh_3)_2]$,[25] $[Ir(CO)(dppe)_2]Cl$,[26] $[Ir(dppe)_2]Cl$,[27] and $Tl[B_3H_8]$ {*via* $[Na(B_3H_8)(C_4H_8O_2)_3]$}[28] were prepared by published methods. The n.m.r. experiments were carried out on solutions in $CDCl_3$ or CD_2Cl_2 using a Bruker HFX-90 instrument modified for pulsed Fourier-transform spectroscopy or using a JEOL FX-100 instrument. Chemical shifts are quoted to high frequency (low applied field) of the reference standards $SiMe_4$ (for ^{1}H), $OEt_2{\cdot}BF_3$ (for ^{11}B), and 85% H_3PO_4 (for ^{31}P). Infrared spectra were recorded for KCl or KBr discs using a Perkin-Elmer 457 grating spectrometer. In the initial experiments the borane–Lewis base adducts B_3H_7L, $B_2H_4L_2$, and BH_3L were identified after their isolation by fractional crystallization and/or column chromatography, and in subsequent experiments by n.m.r. and i.r. spectroscopy together with analytical thin-layer chromatography (t.l.c.); these adducts are well known and their physical and spectroscopic properties have been reported elsewhere.[8,9,12,14,29–34] In the chromatographic experiments benzene–hexane mixtures were used as eluting media and silica gel (100—200 mesh) (Hopkin and Williams) as the stationary phase in the column chromatographs; Kieselgel (type 60; Merck) was used in the t.l.c. experiments, which were used both to analyze mixtures and to monitor the column chromatographs.

Reaction of $[NMe_4][B_3H_8]$ *with* $[CoCl_2(PPh_3)_2]$.—$[NMe_4][B_3H_8]$ (0.96 g; 8.35 mmol) and $[CoCl_2(PPh_3)_2]$ (5.2 g; 8.0 mmol) were stirred with CH_2Cl_2 (80 cm^3) for 24 h at 23 °C. The mixture was filtered, yielding a pale blue precipitate ($[NMe_4]Cl$ and starting material), and the filtrate evaporated to dryness *in vacuo*. Fractional crystallization from C_6H_6–Et_2O and CH_2Cl_2–Et_2O yielded two components, m.p. 185—187 and 189—191 °C, identified by elemental analysis as $BH_3(PPh_3)$ and $B_2H_4(PPh_3)_2$ respectively. Examination of the i.r. and n.m.r. spectra of the initial reaction product indicated that these were the only two borane-containing products. A similar reaction for 72 h in $(CH_3)_2CO$ at 23 °C using $[CoCl_2(PMePh_2)]$ gave the previously unreported compound $BH_3(PMePh_2)$ [m.p. 178—182 °C, ν(B–H) at 2 380s and 2 250w cm^{-1}, δ(^{11}B) −38.0 p.p.m., $^{1}J(^{31}P-^{11}B)$ = 51 Hz, $^{1}J(^{11}B-^{1}H)$ = 91 Hz] as the major borane-containing product.

Reaction of $[NMe_4][B_3H_8]$ *with* $[CoBr(PPh_3)_3]$.—The compounds $[NMe_4][B_3H_8]$ (0.14 g, 1.2 mmol) and $[CoBr(PPh_3)_3]$ (1.08 g, 1.2 mmol) were stirred in CH_2Cl_2 (30 cm^3) for 72 h at 20 °C, and the mixture then filtered. The filtrate was evaporated to dryness and was shown by i.r. and n.m.r. spectroscopy and t.l.c. analysis to have $BH_3(PPh_3)$ as the only borane-containing species present.

Reaction of $Tl[B_3H_8]$ *with* $[CoCl_2(NC_5H_5)_2]$.—The compounds $Tl[B_3H_8]$ (0.98 g, 4.05 mmol) and $[CoCl_2(NC_5H_5)_2]$ (0.57 g, 1.98 mmol) were stirred in tetrahydrofuran (thf) (40 cm^3) for 48 h at *ca*. 20 °C. Filtration yielded a black solid (1.37 g) and a pale green solution; evaporation of the latter yielded a clear viscous oil which was shown by i.r. and integrated n.m.r. spectroscopy to consist of approximately equimolar quantities of $BH_3(NC_5H_5)$ and $B_3H_7(NC_5H_5)$.

Reaction of $[B_3H_8]^-$ *with* I_2 *in the Presence of Lewis Bases.*—The following reaction is typical. Iodine (0.30 g, 1.18 mmol) in monoglyme (10 cm^3) was added slowly over a period of 0.3 h to a stirred suspension of PPh_3 (0.60 g, 2.3 mmol) and $Tl[B_3H_8]$ (0.51 g, 2.08 mmol) in monoglyme (10 cm^3). There was vigorous effervescence and a yellow precipitate (TlI) formed. The more volatile components were removed *in vacuo*, and the solid extracted with benzene; addition of hexane precipitated a white solid which was shown (see above) to consist of $B_3H_7(PPh_3)$ and $BH_3(PPh_3)$.

Reaction of $Tl[B_3H_8]$ *with* trans-$[Ir(CO)Cl(PPh_3)_2]$.—The compounds $Tl[B_3H_8]$ (0.20 g; 0.78 mmol) and *trans*-$[Ir(CO)Cl(PPh_3)_2]$ (0.62 g, 0.78 mmol) were stirred in C_6H_6 (40 cm^3) at *ca.* 20 °C for 48 h, during which time the yellow solution became red-brown. The resulting solid TlCl was filtered off, and the filtrate reduced in volume to *ca.* 15 cm^3 and stored at *ca.* 5 °C for 12 h; the cold solution was filtered, and the solid product washed with cold benzene (3 × 5 cm^3) and diethyl ether (3 × 5 cm^3). It was recrystallized from benzene yielding 1-*carbonyl*-1-*hydrido*-1,1-*bis*(*triphenylphosphine*)-1-*irida*-nido-*tetraborane*, $[(IrB_3H_7)(CO)H(PPh_3)_2]$, as a white, reasonably air-stable solid, m.p. 150—153 °C (decomp.) (0.25 g, 40%) (Found: C, 55.9; H, 4.65; B, 3.8; P, 8.25. $C_{37}H_{38}B_3IrOP_3$ requires C, 56.5; H, 4.85; B, 4.1; P, 7.9%); spectroscopic properties are presented in the Figures and the Table and are discussed in the text. The mother liquor was shown by i.r. and n.m.r. spectroscopy and t.l.c. analysis to contain substantial amounts of $BH_3(PPh_3)$. No reaction was observed when $[NMe_4][B_3H_8]$ was used instead of the thallium(I) salt.

Reaction of $Tl[B_3H_8]$ *with* trans-$[Rh(CO)Cl(PPh_3)_2]$.—The compounds $Tl[B_3H_8]$ (0.12 g, 0.49 mmol) and *trans*-$[Rh(CO)Cl(PPh_3)_2]$ (0.30 g, 0.44 mmol) were stirred in C_6H_6 (30 cm^3) for 4 h at *ca.* 20 °C, during which time the yellow solution became red-brown. The mixture was filtered, and the more volatile components removed from the filtrate *in vacuo*. Infrared and n.m.r. spectroscopy of the residue, together with t.l.c. analysis, showed that $BH_3(PPh_3)$ and $B_3H_7(PPh_3)$ were the only two borane-containing components present.

Reaction of $[NMe_4][B_3H_8]$ *with* $[Ir(CO)(dppe)_2]Cl$.—The compound $[Ir(CO)(dppe)_2]Cl$ (0.60 g, 0.57 mmol) in MeOH (10 cm^3) was added to $[NMe_4][B_3H_8]$ (0.065 g, 0.57 mmol) in MeOH (30 cm^3) at *ca.* 20 °C; a pale yellow precipitate started to form after a few minutes, and after *ca.* 0.5 h this was filtered off and purified by reprecipitation from $CHCl_3$–MeOH to yield $[Ir(CO)(dppe)_2][B_3H_8]$ (0.40 g, 67%) (Found: C, 60.0; H, 5.75; B, 3.3; P, 11.5. $C_{53}H_{56}B_3IrOP_4$ requires C, 60.3; H, 5.35; B, 3.1; P, 11.7%). The identity of the ions $[Ir(CO)(dppe)_2]^+$ and $[B_3H_8]^-$ [35,36] was established by n.m.r. spectroscopy, and the i.r. spectrum was also consistent with the ionic formulation.

Reaction of $[NMe_4][B_3H_8]$ *with* $[Ir(dppe)_2]Cl$.—The compound $[NMe_4][B_3H_8]$ (0.065 g, 0.57 mmol) was added to a solution of $[Ir(dppe)_2]Cl$ (0.55 g, 0.53 mmol) in MeOH (30 cm^3) and the mixture stirred for 1 h at *ca.* 20 °C, during which time the initially red solution became pale yellow. The solvent was removed slowly until an off-white precipitate was formed. This was filtered off and purified by reprecipitation from $CHCl_3$–Et_2O to yield $[Ir(dppe)_2H_2][B_3H_8]$ (0.19 g, 35%) (Found: C, 57.9; H, 5.5; B, 2.5; P, 11.8. $C_{52}H_{58}B_3IrP_4$ requires C, 60.4; H, 5.7; B, 3.1; P, 12.0%). The identity of the ions $[Ir(dppe)_2H_2]^+$ and $[B_3H_8]^-$ was established by n.m.r. spectroscopy,[35,37] and the i.r. spectrum was also consistent with the ionic formulation.

We thank I. M. Ward for some preliminary experimental studies on the systems, A. Hedley for microanalyses, and the S.R.C. for support.

[9/188 *Received, 7th February,* 1979]

REFERENCES

[1] S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, 1968, **7**, 1051; S. J. Lippard and K. M. Melmed, *ibid.*, 1969, **8**, 2755; F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *ibid.*, 1968, **7**, 2272; E. L. Muetterties, W. G. Peet, P. A. Wegner, and C. W. Alegranti, *ibid.*, 1970, **9**, 2447; J. Borlin and D. F. Gaines, *J. Amer. Chem. Soc.*, 1972, **94**, 1367; J. C. Calabrese, D. F. Gaines, S. J. Hildebrandt, and J. H. Morris, *ibid.*, 1976, **98**, 5489.

[2] D. F. Gaines and S. J. Hildebrandt, *J. Amer. Chem. Soc.*, 1976, **96**, 5574.

[3] S. J. Hildebrandt, D. F. Gaines, and J. C. Calabrese, *Inorg. Chem.*, 1978, **17**, 790.

[4] V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 1973, **95**, 5078; 1976, **98**, 1600; L. G. Sneddon and D. Voel, *J.C.S. Chem. Comm.*, 1976, 118; V. R. Miller, R. Weiss, and R. N. Grimes, *J. Amer. Chem. Soc.*, 1977, **99**, 5646; J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, 1977, **16**, 3251, 3255.

[5] M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante, and S. S. Wreford, *J. Amer. Chem. Soc.*, 1974, **96**, 4042; M. R. Churchill and J. J. Hackbarth, *Inorg. Chem.*, 1975, **14**, 2047; R. W. Marks, S. S. Wreford, and D. D. Traficante, *ibid.*, 1978, **17**, 756.

[6] N. N. Greenwood, J. D. Kennedy, W. S. McDonald, D. Reed, and J. Staves, *J.C.S. Dalton*, 1979, 117.

[7] I. M. Ward, Ph.D. Thesis, University of Leeds, 1975.

[8] B. M. Graybill and J. K. Ruff, *J. Amer. Chem. Soc.*, 1962, **84**, 1062.

[9] W. Van Doorne, A. W. Cordes, and C. W. Hunt, *Inorg. Chem.*, 1973, **12**, 1686.

[10] P. J. Dolan, J. H. Kinsvater, and D. G. Peters, *Inorg. Chem.*, 1976, **15**, 2170.

[11] B. G. Cooksey, J. D. Gorham, J. H. Morris, and L. Kane, *J.C.S. Dalton*, 1978, 141.

[12] J. H. Morris and A. Drummond, *Inorg. Chim. Acta*, 1977, **24**, 191.

[13] N. N. Greenwood, J. D. Kennedy, and D. Reed, unpublished work.

[14] K. C. Naiman and G. E. Ryschkewitsch, *Inorg. Chem.*, 1969, **8**, 2671.

[15] G. W. Schaeffer and E. R. Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 2143.

[16] D. F. Gaines and S. J. Hildebrandt, *Inorg. Chem.*, 1978, **17**, 794.

[17] C. H. Bushweller, H. Beald, M. Grace, W. J. Dewkett, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, 1971, **93**, 2145; D. W. Lowman, P. D. Ellis, and J. D. Odom, *J. Magnetic Reson.*, 1972, **8**, 289.

[18] A. R. Kane and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 1041.

[19] L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 5665.

[20] I. M. Pepperberg, T. A. Halgren, and W. N. Lipscomb, *Inorg. Chem.*, 1977, **16**, 363.

[21] N. N. Greenwood, W. S. McDonald, D. Reed, and J. Staves, *J.C.S. Dalton*, 1979, 1339.

[22] M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 1969, **3**, 227.

[23] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1961, 285.

[24] E. G. Cox, A. J. Shorter, W. Wardlaw, and W. J. R. Way, *J. Chem. Soc.*, 1937, 1536.

[25] J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Synth.*, 1968, **11**, 101.

[26] L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, 1966, **88**, 5324.

[27] A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Comm.*, 1966, 589.

[28] E. M. Amberger and E. Gut, *Chem. Ber.*, 1968, **101**, 1200.

[29] M. D. Taylor, L. R. Grant, and C. A. Sands, *J. Amer. Chem. Soc.*, 1955, **77**, 1506.

[30] L. J. Edwards, W. V. Hough, and M. D. Ford, *Angew. Chem.*, 1957, **69**, 678.

[31] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 4496.

[32] M. A. Ring, E. Witucki, and R. C. Greenhough, *Inorg. Chem.*, 1967, **6**, 395.

[33] R. T. Paine and R. W. Parry, *Inorg. Chem.*, 1972, **11**, 268.

[34] J. D. Glore, J. Rathke, and R. Schaeffer, *Inorg. Chem.*, 1973, **12**, 2175.

[35] D. Marynick and T. Onak, *J. Chem. Soc. (A)*, 1970, 1160.

[36] K. G. Caulton and J. S. Miller, *J. Amer. Chem. Soc.*, 1975, **97**, 1067.

[37] M. J. Hopkinson and J. F. Nixon, *J. Organometallic Chem.*, 1978, **148**, 201.