Electrolysis of Borane Anions at Reactive Metal Anodes: A Convenient Route to Metallaboranes

By **Brian G. Cooksey, John D. Gorham, John H. Morris,*** and (in part) **Lorna Kane,** Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL

Electrolysis of non-aqueous solutions of octahydrotriborate(1−) salts at copper or silver anodes in the presence of phosphine ligands leads to metal dissolution, and formation of metallaboranes. Metal dissolution occurs with zinc or cadmium anodes, but the complexes are cleaved by phosphine ligands.

ELECTROLYSIS of tetrahydroborate salts has previously been used as a method of preparing diborane [1] and borane derivatives,[2] and has received only brief attention as a route for preparing solvated magnesium or calcium tetrahydroborate.[3] The octahydrotriborate(1−) anion has recently been shown to undergo electrochemical oxidation at a platinum or gold anode to give $MeCN\cdot B_3H_7$ or $HCONMe_2\cdot B_3H_7$.[4]

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[1] R. K. Birdwhistell, H. E. Ulmer, and L. L. Quill, U.S.P., 2,879,179/1959; W. H. Schechter, U.S.P., 3,033,766/1962; E. B. Baker, R. B. Ellis, and W. S. Wilcox, *J. Inorg. Nuclear Chem.*, 1961, **23**, 41; R. M. Adams, *Adv. Chem. Ser.*, 1961, **32**, 60.

[2] R. S. Tinsley, *Diss. Abs.*, 1959, **19**, 2890; W. H. Schechter, R. M. Adams, and G. F. Huff, B.P., 826,558/1960; L. A. Melcher, I. A. Boenig, and K. Niedenzu, *Inorg. Chem.*, 1973, **12**, 487.

[3] G. F. Huff, A. D. McElroy, and R. M. Adams, U.S.P., 2,855,353/1958.

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

RESULTS

We now report that metal derivatives of the small anions tetrahydroborate(1−), $[BH_4]^-$, and octahydrotriborate(1−), $[B_3H_8]^-$, are conveniently prepared by electrolysis at reactive metal anodes in a range of organic solvents.

Copper Anode.—The well known [5] compound $[Cu(BH_4)(PPh_3)_2]$ was easily prepared by electrolysis at a copper anode of a solution of $Na[BH_4]$ in ethanol containing PPh_3. Similarly, $[Cu(B_3H_8)(PPh_3)_2]$ [5,6] was prepared by electrolysis at a copper anode of solutions of octahydrotriborate(1−) salts in either MeCN or CH_2Cl_2 containing PPh_3. When the ligand present was $PEtPh_2$ a solution of the phosphinecopper octahydrotriborate, which was thermally unstable at room temperature, was formed. Electrolysis of octahydrotriborate salts at a copper anode at low temperatures *without* phosphine ligands produced copper-containing solutions which were stable at −78 °C but unstable at room temperature.

Silver Anode.—Electrolysis of $[NMe_4][B_3H_8]$ in MeCN containing PPh_3 using a silver anode resulted in the precipitation of the new silver derivative $[Ag(B_3H_8)(PPh_3)_3]$. The only stable silver octahydrotriborate derivatives previously reported are of the type $[Ag(B_3H_8)L_2]$.[6]

Zinc and Cadmium Anodes.—Electrolysis of octahydrotriborate(1−) salts at either zinc or cadmium anodes in methylene chloride or acetonitrile in the presence of PPh_3 resulted in metal dissolution, but the only identifiable products were $Ph_3PB_3H_7$ and its cleavage products Ph_3PBH_3 and $(Ph_3P)_2B_2H_4$. Metal dissolution also occurred in the absence of ligand.

Platinum Anode.—Electrolysis of $[B_3H_8]^-$ at a platinum anode in the presence of PPh_3 led only to $Ph_3PB_3H_7$, Ph_3PBH_3, and $(Ph_3P)_2B_2H_4$ without metal dissolution.

DISCUSSION

Method.—The preparation of metallaboranes by electrochemical methods offers advantages over standard metathetical routes in that the normal thermodynamic principles governing the formation of compounds (high lattice energy of alkali halides, or insolubility of one or more species) can be circumvented, and thus salts of borane anions with large cations may be used with the following advantages. Such salts are often thermally much more stable than their simple alkali-metal counterparts, have good solubilities in weakly polar solvents, and give poor yields of products when involved in metathetical reactions. It should therefore be possible to prepare metallaboranes by the electrochemical method which are inaccessible by alternative routes.

Electrochemical Behaviour of the Copper Anode.—The factors governing the dissolution of metal anodes have not yet been fully established. Few electrode potentials in non-aqueous media have been reported, and extrapolations of data from standard potentials (aqueous media) to non-aqueous systems with or without added ligands may be only a rough guide to the behaviour in non-aqueous systems. We have found that dissolution of metal from a copper anode in acetonitrile, methylene chloride, or ethanol occurs in preference to oxidation of $[B_3H_8]^-$ or $[BH_4]^-$, in the presence or absence of triphenylphosphine ligand. A non-reversible polarographic wave for oxidation of $[B_3H_8]^-$ occurred at a half-wave potential of *ca.* +0.6 V with respect to the standard calomel electrode (s.c.e.) in acetonitrile, which is consistent with the chronopotentiometric oxidation value of *ca.* +0.4 V *versus* Ag–AgCl reported by Dolan *et al.*[4] The standard potential for the Cu^+–Cu system is reported to be 0.52 V (aqueous) and −0.38 V (MeCN).[7] A preliminary study of the electrode potentials for the system $(Ph_3P)_2CuB_3H_8$–$[NBu_4]$–$[B_3H_8]$–Cu in MeCN or CH_2Cl_2 showed a complicated behaviour. However, the potentials recorded were in the range −0.6 to −0.7 V in MeCN and −0.8 to −0.9 V in CH_2Cl_2 with respect to a reference electrode * consisting of Ag–0.1 mol dm^{-3} $Ag[NO_3]$–0.1 mol dm^{-3} $Na[ClO_4]$ in each solvent.[8] Since the product isolated from electrolysis at the copper anode was the well known compound $[Cu(B_3H_8)(PPh_3)_3]$, in which the copper is co-ordinated to both phosphine and $[B_3H_8]^-$ ligands,[9] the chelating ability of the borane anion undoubtedly plays an important role in dissolution of the metal. It appears likely that the species first produced at the electrode was $[Cu(B_3H_8)]$ which subsequently interacted with any ligand present. In the absence of phosphine ligands, copper dissolution still took place but the nature of the species produced has not yet been fully established. In acetonitrile the species was strongly ionised since the current remained approximately constant during the course of the electrolysis, whereas in methylene chloride the current decreased with time. It is possible that a species such as $[Cu(B_3H_8)_2]^-$ was produced. The probable scheme is as in equation (1).

$$Cu \xrightarrow[-e^-]{[B_3H_8]^-} [Cu(B_3H_8)] \xrightarrow{L} [Cu(B_3H_8)L_2] \quad (L = PPh_3 \text{ or } PEtPh_2) \qquad (1)$$

Silver Anode and Products.—Muetterties *et al.*[6] reported the preparation of a stable complex of the type $[Ag(B_3H_8)L_2]$ with the ligand $P(C_6H_4Me\text{-}p)_3$, and suggested that the borane anion is bound to the silver without necessarily implying a crystallographic structure similar to the copper complex. Our observation that electrolysis at a silver electrode led to silver dissolution is consistent with this interaction; on the basis of standard-potential data alone, it might have been expected that oxidation of the $[B_3H_8]^-$ ion would occur in preference to metal dissolution. Furthermore, we found that, with the ligand PPh_3, the crystalline phase obtained was $[Ag(B_3H_8)L_3]$, and a measurement of the equivalent

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* The potential of the electrode, measured with respect to the s.c.e., was found to be 0.3 V in MeCN and 0.41 V in CH_2Cl_2.

[5] S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, 1968, **7**, 1051, and refs. therein.

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[8] R. C. Larson, R. T. Iwamoto, and R. N. Adams, *Analyt. Chim. Acta*, 1961, **25**, 371.

[9] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1969, **8**, 2755.

conductance showed that this compound ionised significantly in CH_2Cl_2 solution. However, the room-temperature ^{11}B n.m.r. spectrum showed no resolvable coupling and therefore significant $M-B_3H_8$ interaction must occur. Muetteties *et al.*[6] found that, with their ligand, a species of composition $[Ag(B_3H_8)L_3]$ dissociated in solution to give an equilibrium mixture of $[Ag(B_3H_8)L_2]$, $[Ag(B_3H_8)L_3]$, and $[AgL_4][B_3H_8]$.

The reason for the different behaviour of the two closely related ligands is not fully established; it may be that crystal-packing factors dominate, and determine whether $[Ag(B_3H_8)L_2]$ or $[Ag(B_3H_8)L_3]$ is formed in the solid state. The overall scheme is therefore as in (2).

TABLE 1

Typical experimental conditions

Experiment no.	Anode	Solvent	Amount (g) of $[B_3H_8]^-$ salt	Cation	Amount of ligand (g)	Charge passed (Q/C)	Anode weight loss (g)	Percentage of anode consumed [a]
1	Cu	CH_2Cl_2 [b]	2.0	$[NBu_4]^+$	3.7 [c]	463	0.283	93
2	Cu	MeCN [d]	1.0	$[NMe_4]^+$ [e]	3.7 [f]	*g*	0.50	*g*
3	Cu	MeCN [h]	1.0	$[NMe_4]^+$ [e]		1 192	0.86	91
4	Cu	EtOH	0.29	Na^+	4.0 [c]	144	0.1	105
5	Ag	MeCN [d]	2.0	$[NBu_4]^+$ [j]	3.7 [c]	517	0.60	103
6	Pt	CH_2Cl_2	2.0	$[NBu_4]^+$	3.7 [c]	659	0	0
7	Zn	MeCN [d]	1.0	$[NMe_4]^+$ [e]	2.3 [c]	*g*	0.08	9
8	Zn	CH_2Cl_2	2.0	$[NBu_4]^+$		*g*	*g*	*g*
9	Cd	MeCN	2.3	$[NMe_4]^+$	5.2 [c]	*g*	*g*	*g*

[a] Based on current passed. [b] Similar results were obtained with MeCN. [c] PPh_3. [d] Similar results were obtained with CH_2Cl_2. [e] Similar results were obtained with $[NBu_4]^+$ and $[N(PPh_3)_2]^+$. [f] $PEtPh_2$. [g] Not measured accurately. [h] -20 °C. [i] $[BH_4]^-$. [j] Similar results were obtained with $[NMe_4]^+$ or $[N(PPh_3)_2]^+$.

TABLE 2

Analytical data on selected products

Experiment no.	Product	Analysis (%) Found C	H	P	B	M	Calculated C	H	P	B	M
1	$[Cu(B_3H_8)(PPh_3)_2]$	67.8	6.15			9.95	68.8	6.10			10.1
4	$[Cu(BH_4)(PPh_3)_2]$	72.3	5.75	10.4			71.7	5.70	10.25		
5	$[Ag(B_3H_8)(PPh_3)_3]$	69.25	5.55	9.85	3.60	10.2	69.35	5.70	9.95	3.45	11.55
7	$(Ph_3P)_2B_2H_4$	78.65	6.40				78.6	6.25			

$$Ag \xrightarrow[-e^-]{[B_3H_8]^-} [Ag(B_3H_8)] \xrightarrow{PPh_3} [Ag(B_3H_8)(PPh_3)_3] \qquad (2)$$

Platinum, Zinc, and Cadmium Anodes.—In view of the fact that copper and silver anodes led to metallaboranes for which there were known analogues, it was of interest to re-examine the electrolysis of the $[B_3H_8]^-$ anion in the presence of PPh_3 at a platinum electrode, since it had previously been reported that platinum formed a complex, $[Pt(B_3H_7)L_2]$, with PPh_3.[10] We were unable to detect metal dissolution, but instead found oxidation of $[B_3H_8]^-$ to LB_3H_7 and its subsequent cleavage products LBH_3 and $L_2B_2H_4$ with PPh_3.[11]

Metal dissolution might reasonably be expected from the more electropositive elements zinc and cadmium, although there are no $[B_3H_8]^-$ derivatives reported in the literature. We observed this dissolution, but the metallaboranes produced were unstable in the presence of PPh_3, resulting in cleavage, precipitation of grey metal-containing deposits, and isolation of the adducts Ph_3PBH_3 and $(Ph_3P)_2B_2H_4$.

EXPERIMENTAL

Solvents and Reagents.—Acetonitrile and CH_2Cl_2 were purified and dried according to the literature.[12] Tetramethylammonium octahydrotriborate was purchased from Strem Chemicals Inc.; $[NBu_4][B_3H_8]$ and $[N(PPh_3)_2][B_3H_8]$ were prepared by the reported methods;[13] all the solid reagents were dried *in vacuo* before use.

Electrolytic Method.—Simple two-compartment cells were used in which the anode compartment of *ca.* 100 cm^3 capacity was separated from a smaller co-axial cathode compartment by a glass sinter. The anode compartment was stirred magnetically, and the cathode comprised a layer of mercury (*ca.* 20 cm^3) covering the sinter. Some cells were designed so that both the anode and cathode compartments could be evacuated simultaneously; others were designed so as to be demountable, or with a water-cooled jacket. The power supply was an Advance Electronics BRM 60–03 giving a constant current or constant voltage. The current was monitored by means of a chart recorder measuring the voltage drop across a Decade resistance box in series with the cell. The applied voltage depended on the solvent being used, and the appearance of oxidised solvent products in the anode compartment; in general, the potential was *ca.* 5.4 V in MeCN and 20—60 V for CH_2Cl_2 and EtOH.

Electrolyses.—Typical experimental conditions are given in Table 1. The products from selected experiments were recrystallised, and their analytical data are given in Table 2. Further confirmation of product identity was obtained from i.r. and ^{11}B n.m.r. spectra.

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[13] *Inorg. Synth.*, 1974, **15**, 111.

The i.r. and ^{11}B n.m.r. spectra of $[Cu(B_3H_8)(PPh_3)_2]$ at room temperature agreed with the literature.[5] The i.r. spectrum of $[Cu(BH_4)(PPh_3)_2]$ (experiment 7) in the B–H stretching region showed bands at 2 400, 2 360(sh), 2 300, and 2 240 cm^{-1} (terminal), and 2 010 and 1 960 cm^{-1} (bridging), the latter two bands shifting to 1 983 and 1 920 cm^{-1} after recrystallising from acetone–ethanol. The ^{11}B n.m.r. spectrum comprised a poorly resolved quintet [δ −28 p.p.m.; J(B–H) 80 Hz]. The ^{11}B n.m.r. spectra of the solutions obtained in experiments 2 and 3 showed a single broad line near δ −33 p.p.m. which began to show resolution after prolonged storage at room temperature (metallic Cu precipitated out). The i.r. spectrum of $[Ag(B_3H_8)(PPh_3)_3]$ (experiment 5) had bands in the B–H stretching region which were similar in appearance to those of $[N(PPh_3)_2][B_3H_8]$, and differed considerably from $[Cu(B_3H_8)(PPh_3)_2]$. The ^{11}B n.m.r. spectrum in CH_2Cl_2 comprised a single broad line (δ −32 p.p.m.). The equivalent conductance (CH_2Cl_2 at 20 °C) was 3.4 Ω^{-1} cm^2 equivalents^{-1} for a solution of concentration 5×10^{-3} equivalents l^{-1}. The ^{11}B n.m.r. spectrum of the freshly prepared solution from experiment 6 contained broad signals in the ratio 2 : 1 at δ −16.1 and −45.8 p.p.m., corresponding to $Ph_3PB_3H_7$,[14] in addition to unchanged $[B_3H_8]^-$ (δ −30.1 p.p.m.). The solution on storage gave superimposed ^{11}B signals associated with Ph_3PBH_3 and $(Ph_3P)_2B_2H_4$. In the products isolated from experiments 7—9, $Ph_3PB_3H_7$, Ph_3PBH_3, and $(Ph_3P)_2B_2H_4$ were identified by their i.r. and ^{11}B and ^{31}P n.m.r. spectra.

Spectroscopic Techniques.—The i.r. spectra were recorded as mulls in Nujol or hexachlorobutadiene on a Perkin-Elmer 457 grating spectrometer. The ^{11}B and ^{31}P n.m.r. spectra were obtained on a JEOL-PS-100-PFT-100 spectrometer operated at 25.15 MHz, utilising the ^{13}C probe and operating unlocked at reduced field strength. Chemical shifts are quoted on the recently adopted convention (3rd I.M.E. Boron Conference, Ettal, July 1976) that positive shifts are to low field. References were $OEt_2 \cdot BF_3$ (capillary or external; slight differences are observed between these) or $P(OMe)_3$ (external).

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