The electrooxidation of the tetraphenylborate ion revisited

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Received (in Montpellier, France) 17th July 2001, Accepted 12th November 2001
First published as an Advance Article on the web

The electrochemistry of the tetraphenylborate ion, BPh_4^-, has been studied by cyclic voltammetry and coulometry in water, methanol, ethanol, acetonitrile, acetone, dimethylformamide and dichloromethane under an N_2 atmosphere. While a one-electron and somewhat irreversible oxidation (with an $E_{1/2}$ of 0.87 V *vs.* SCE at a glassy carbon electrode) is observed in dichloromethane, eqn. (i),

$$BPh_4^- \rightleftharpoons {}^{\bullet}BPh_4 + e^- \qquad \text{(i)}$$

the oxidation is somewhat complicated in all other solvents by the occurrence of several consecutive reactions. E_{pa}, the anodic peak potential in cyclic voltammetry, changes from 0.41 V *vs.* SCE in water to 0.94 V *vs.* SCE in dimethylformamide at a glassy carbon electrode. The variation in E_{pa} with solvent (S) is explained by invoking reaction (ii).

$${}^{\bullet}BPh_4 + S \rightarrow S\text{–}BPh_3 + {}^{\bullet}Ph \qquad \text{(ii)}$$

The coulometric results in solvents other than dichloromethane indicate a disproportionation of $S\text{–}BPh_3$, eqn. (iii).

$$2S\text{–}BPh_3 \rightarrow S\text{–}BPh_2^+ + BPh_4^- + S \qquad \text{(iii)}$$

Geske[1] has previously examined the electrochemical behaviour of the tetraphenylborate ion (BPh_4^-) in acetonitrile by both voltammetry and coulometry. From voltammetry experiments in acetonitrile using a rotating platinum microelectrode, he found that BPh_4^- undergoes an irreversible two-electron oxidation according to eqn. (1) around 0.8 V *vs.* a $Ag/AgNO_3$ electrode.

$$BPh_4^- \rightarrow BPh_2^+ + Ph\text{–}Ph + 2e^- \qquad (1)$$

From coulometry experiments in acetonitrile he observed that the number of electrons transferred depends on the concentration of BPh_4^-; as the concentration of BPh_4^- is decreased, then the number of electrons being transferred becomes closer to two. A full two-electron count could only be obtained in the presence of a buffer.[1] From these observations he suggested that electrode process (1) is followed by a secondary chemical reaction involving a proton, eqn. (2), which consumes BPh_4^-.

$$BPh_4^- + H^+ \rightarrow BPh_3 + PhH \qquad (2)$$

The proton involved in eqn. (2) is generated by the interaction of BPh_2^+ and the solvent [eqn. (3)].

$$BPh_2^+ + CH_3CN \rightarrow Ph_2BCH_3CN^+ \rightarrow Ph_2BCH_2CN + H^+ \qquad (3)$$

However, prior to Geske, Wittig and Raff[2] observed that in diethyl ether reaction (4)

$$2LiBPh_4 + 2CuCl_2 \rightarrow 2CuCl + 2LiCl + 2BPh_3 + Ph\text{–}Ph \qquad (4)$$

occurs where BPh_4^- acts as a one-electron reductant. With the hope of observing a one-electron redox process for BPh_4^- in a solvent of low dielectric constant, we have studied its electrochemistry by cyclic voltammetry and coulometry in several common solvents. The results are reported here.

Results and discussion

We have performed cyclic voltammetry measurements on the tetrabutylammonium (Bu_4N^+) salt of BPh_4^- in dichloromethane at a Pt electrode as well as at a glassy carbon (GC) electrode under an N_2 atmosphere using Bu_4NClO_4 as the supporting electrolyte. At a scan rate v of 50 mV s^{-1}, only an anodic peak is observed on the positive side of the saturated calomel electrode (SCE) (Fig. 1); however, at higher scan rates,

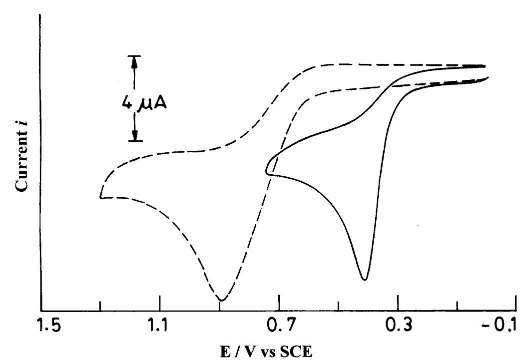


Fig. 1 Cyclic voltammograms of $NaBPh_4$ in water (full line; concentration $c = 1.08$ mmol dm^{-3}) and of Bu_4NBPh_4 in CH_2Cl_2 (broken line; $c = 1.04$ mmol dm^{-3}) at a glassy carbon electrode under N_2 atmosphere at $v = 50$ mV s^{-1}. Supporting electrolyte: 0.1 mol dm^{-3} $NaClO_4$ in water and 0.1 mol dm^{-3} Bu_4NClO_4 in CH_2Cl_2.

DOI: 10.1039/b106356c

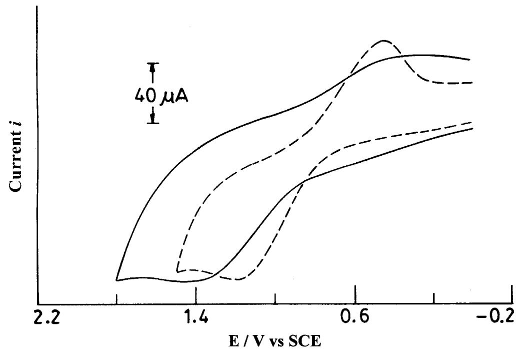


Fig. 2 Cyclic voltammograms of Bu_4NBPh_4 in CH_2Cl_2 at $v = 5000$ mV s^{-1} at a glassy carbon electrode (full line) and at a platinum electrode (broken line) under N_2 atmosphere. ($c = 0.87$ mmol dm^{-3}. Supporting electrolyte: 0.1 mol dm^{-3} Bu_4NClO_4.)

the cathodic peak becomes visible (Fig. 2). The electrode process is less irreversible at a Pt electrode than at a GC electrode (Fig. 2); the peak-to-peak separation (ΔE_p) at $v = 5000$ mV s^{-1} at a Pt electrode is 0.75 V with a half-wave potential $E_{1/2}$ of 0.82 V *vs.* SCE and at a GC electrode the ΔE_p at $v = 5000$ mV s^{-1} is 1.04 V with an $E_{1/2}$ of 0.87 V *vs.* SCE. In coulometry at a Pt wire gauge electrode in CH_2Cl_2 under N_2 atmosphere only one electron is transferred (Table 1). Thus,

Table 1 Coulometric data for BPh_4^- in some solvents (S) at a Pt wire gauge electrode[a]

S	*c*	*n*
CH_2Cl_2	0.426	0.97
	1.040	1.04
Acetone	0.434	1.68
	1.054	1.56
Acetonitrile	0.441	1.60
	1.052	1.28
DMF	0.437	1.69
	0.991	1.40

[a] $NaBPh_4$ was electrolysed in acetone, acetonitrile and DMF while Bu_4NBPh_4 was electrolysed in CH_2Cl_2; in acetone, acetonitrile and DMF $NaClO_4$ was used as the supporting electrolyte and in CH_2Cl_2 the supporting electrolyte was Bu_4NClO_4. *c* is the concentration of BPh_4^- in the electrolysed solution in mmol dm^{-3} (total volume of the solution in each case was 25 ml) and *n* is the number of electrons transferred in coulometry.

the electrode process observed in dichloromethane is given by eqn. (5).

$$^{\bullet}BPh_4 + e^- \rightleftharpoons BPh_4^- \quad (5)$$

The cyclic voltammetry study of the sodium salt of BPh_4^- in water, methanol, ethanol, acetone, acetonitrile and dimethylformamide (DMF) was performed also at a GC electrode under an N_2 atmosphere using $NaClO_4$ as the supporting electrolyte. In all these solvents BPh_4^- uniformly displays an irreversible voltammogram at the GC electrode on the positive side of SCE with complete absence of the cathodic peak; the anodic peak potential E_{pa} depends on the solvent (Table 2). At a v of 50 mV s^{-1}, E_{pa} is 0.94 V *vs.* SCE in DMF (Table 2) as compared to only 0.41 V *vs.* SCE in water (Fig. 1). Even at a v of 5000 mV s^{-1}, it was not possible to observe the cathodic peaks. A comparison of peak currents with those of the ferrocene–ferrocenium couple under the same experimental conditions indicates that the electrode process involves only one electron.

The one-electron oxidation of BPh_4^- produces the neutral species $^{\bullet}BPh_4$. Consequently, only solvation of BPh_4^- is pertinent here. The volume of BPh_4^- in the solid state has been previously estimated[3] to be 306.6 $Å^3$. Assuming a sphere, this ionic volume yields a radius of 4.18 Å. By use of the Born equation[4,5] this radius indicates that a change of solvent from water (dielectric constant ε at 25 °C = 78.54)[4] to DMF (ε at 25 °C = 37.25)[6] should lead to a decrease of only 0.024 V in E_{pa}. Experimentally, however, an increase of 0.53 V in E_{pa} is observed when going from water to DMF (Table 2).

The variation in E_{pa} of BPh_4^- with solvent can be rationalised if we assume that the primary electrode process (5) is followed by a disintegration of $^{\bullet}BPh_4$ into BPh_3 and $^{\bullet}Ph$, generating a solvato species S–BPh_3 (S: solvent) [eqn. (6)].

$$^{\bullet}BPh_4 + S \rightarrow S\text{–}BPh_3 + {}^{\bullet}Ph \quad (6)$$

If ΔG^0 is the free energy change due to reaction (6), $E_{1/2}$ of couple (5) will decrease as reaction (6) becomes thermodynamically more feasible.[7] We have calculated the heat of reaction ΔH^0 for reaction (6) in the gas phase for the various solvents in the present study by the AM1 method using the standard MOPAC package (version 1.1);[8] the ΔH^0 values are presented in Table 2. It is interesting to note that in the gas phase DMF appears to bind to BPh_3 by the oxygen end rather than by the nitrogen atom. As the number of molecules on both sides of reaction (6) in the gas phase are equal, the entropy factor is expected to be similar for all solvents.[9] Since the cathodic peak for couple (5) is only observed in CH_2Cl_2, we have investigated the possible correlation between $-\Delta H^0$ and E_{pa}, assuming that ΔE_p in all solvents remains comparable

Table 2 Anodic peak potential (E_{pa}) data for BPh_4^- in various solvents (S) at a glassy carbon (GC) electrode and at a Pt electrode; some properties of the solvents, calculated ΔH^0 values for reaction (6) in the gas phase and association constant (K_a) for Bu_4NBPh_4 in some solvents[a]

				E_{pa}			
S	ε	AN	DN	GC	Pt	ΔH^0	K_a
Water	78.54	54.8	≥18.0	0.41	–[b]	−57.36	–
Methanol	32.63	–	19.0	0.67	–[b]	−27.03	37 ± 4[c]
Ethanol	24.30	37.9	20	0.66	–[b]	−33.76	–
Acetone	20.70	12.5	17.0	0.79	0.84	−16.48	<10[d]
Acetonitrile	35.72[e]	18.9	14.1	0.78	0.85	−21.84	14[f]
DMF	37.52[e]	16.0	26.6	0.94	0.98	−11.42	<10[g]
CH_2Cl_2	8.92[e]	20.4	<10	0.89	0.87	−13.68	3300[h]

[a] Dielectric constants (ε) at 25 °C are taken from ref. 4 unless otherwise specified. Gutmann solvent acceptor numbers (AN) and donor numbers (DN) are taken from ref. 10. For cyclic voltammmetry Bu_4NBPh_4 was used in CH_2Cl_2 and $NaBPh_4$ in all other solvents; Bu_4NClO_4 was used as the supporting electrolyte in CH_2Cl_2 and $NaClO_4$ as the supporting electrolyte in all other solvents. The E_{pa} values were obtained at $v = 50$ mV s^{-1} and are given in V *vs.* SCE. ΔH^0 values are given in kJ mol^{-1} and K_a in mol^{-1} dm^3. [b] No proper cyclic voltammetric response could be obtained. [c] From ref. 17. [d] From ref. 18. [e] From ref. 6. [f] From ref. 19. [g] From ref. 20. [h] From ref. 21.

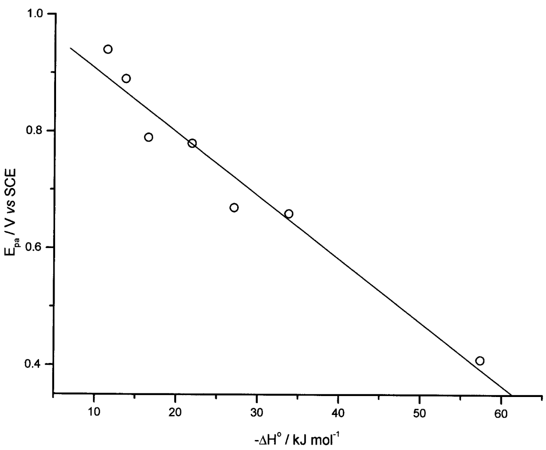


Fig. 3 Correlation of the anodic peak potential E_{pa} of BPh_4^- obtained at a glassy carbon electrode in a variety of solvents with ΔH^0 calculated for reaction (6) in the gas phase. Correlation coefficient $r = 0.978$. For data, see Table 2.

to that observed in CH_2Cl_2. Fig. 3 shows that there exists a satisfactory linear relationship between E_{pa} and $-\Delta H^0$; the lower the value of ΔH^0, the more difficult it is to oxidise BPh_4^-. The slope of the line in Fig. 3 is found to be 0.0108, which is very close to the ideal value of 0.0103, the required factor when converting kJ mol^{-1} to eV.

We have also examined whether the E_{pa} values in various solvents can be explained in terms of Gutmann[10] solvent donor numbers (DN) and acceptor numbers (AN). The experimentally determined parameters DN and AN are respectively the measure of the basicity and acidity of a solvent; the larger the value of DN or AN, the more electron-donating or -accepting is the solvent. Earlier it has been found that the redox potentials of an anionic electroactive species [*e.g.*, $Fe(CN)_6^{3-}$] in various solvents can be correlated with AN while those of a cationic electroactive species [*e.g.*, Na^+] with DN.[11] We have found that the E_{pa} values of our anionic electroactive species BPh_4^- show some sort of linear correlation with AN (Table 2; Fig. 4). Roughly speaking, the anion BPh_4^- is stabilised in solvents of lower AN values, that is in less electron-accepting solvents. This is in line with the earlier observations that anions are more stabilised in less electron-accepting solvents.[10]

Apparently, reaction (6) is so fast that even at a v as high as 5000 mV s^{-1} no trace of the cathodic peak can be observed in cyclic voltammetry in any of the solvents studied except CH_2Cl_2. The phenyl radical that is generated by reaction (6) disappears from the electrode surface by forming biphenyl, eqn. (7).

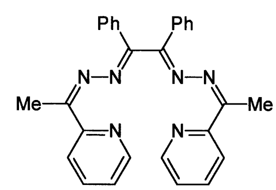
$$Ph^\bullet + {}^\bullet Ph \rightarrow Ph\text{–}Ph \qquad (7)$$

The cyclic voltammetric behaviour of $NaBPh_4$ in all the solvents except CH_2Cl_2 has also been examined at a Pt electrode under N_2 atmosphere using $NaClO_4$ as the supporting electrolyte. We have not been able to observe the oxidation of BPh_4^- in water, methanol or ethanol at a Pt electrode. For other solvents, however, an irreversible oxidation has been observed with complete absence of the cathodic peak, even at a v of 5000 mV s^{-1}. The E_{pa} data are given in Table 2. While current height considerations indicate a one-electron process like couple (5) the coulometric results (under N_2 atmosphere at a Pt wire gauge electrode) are essentially similar to those obtained by Geske[1] in CH_3CN: as the concentration of BPh_4^- is lowered then the number of electrons transferred approaches two (Table 1). It should be mentioned that, as reported by Geske,[1] the electrolysis of $NaBPh_4$ in acetone, acetonitrile and DMF is very slow. To reconcile our cyclic voltammetric and coulometric results in the various solvents with the observations by Geske[1] we propose that in coulometry the species S–BPh_3 disproportionates in a manner shown in eqn. (8) to regenerate BPh_4^-.

$$2S\text{–}BPh_3 \rightarrow S\text{–}BPh_2^+ + BPh_4^- + S \qquad (8)$$

This disproportionation, which obviously depends on the nature of the solvent, does not occur in the weakly coordinating dichloromethane. Hence, the one-electron redox process for BPh_4^- is only observed in CH_2Cl_2.

Finally, we have found that in the copper(I) complex [CuL]BPh_4 (**1**), where L is a 2 : 1 condensate of 2-acetylpyridine and benzil dihydrazone, couple (5) is much less irreversible than for Bu_4NBPh_4 in dichloromethane in cyclic voltammetry at a GC electrode; even at $v = 50$ mV s^{-1} the cathodic peak is quite visible, *cf.* Fig. 5 with Fig. 1. At $v = 50$ mV s^{-1} for **1**, couple (5) in dichloromethane has an $E_{1/2}$ of 0.82 V *vs.* SCE with a ΔE_p of 0.12 V. The quasireversible response around 0.5 V *vs.* SCE in Fig. 5 is due to the electrode process $Cu^{II} + e^- \rightleftharpoons Cu^I$. Incidentally, the perchlorate analogue of **1**, [CuL]ClO_4, displays only the $Cu^{II/I}$ couple.[12]



L

For the sake of completeness of our study we have also carried out an X-ray crystallographic study of [CuL]BPh_4. Direct diffusion of hexane into a moderately concentrated

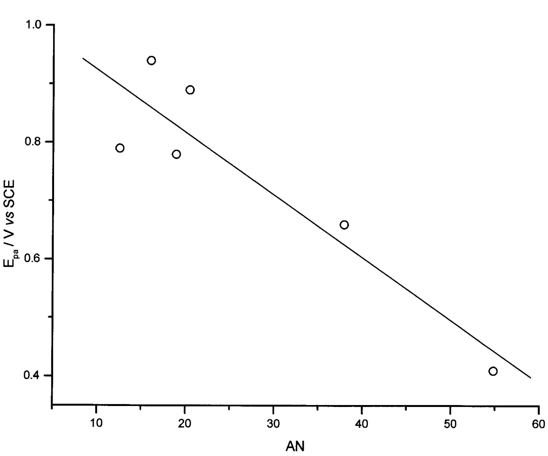


Fig. 4 Correlation of E_{pa} of BPh_4^- obtained at a glassy carbon electrode in a variety of solvents with Gutmann solvent acceptor number AN. $r = 0.918$. For data, see Table 2.

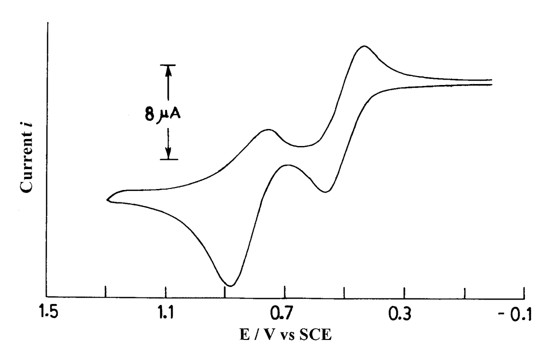


Fig. 5 Cyclic voltammogram of **1** in CH_2Cl_2 at $v = 50$ mV s^{-1} at a glassy carbon electrode under N_2 atmosphere. ($c = 1.46$ mmol dm^{-3}. Supporting electrolyte: 0.1 mol dm^{-3} Bu_4NClO_4.)

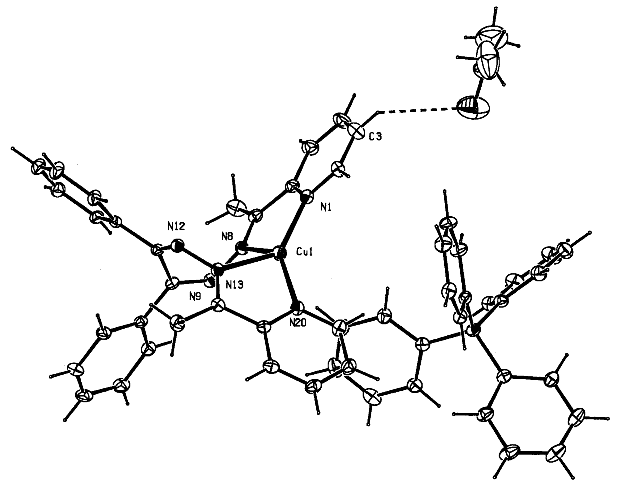


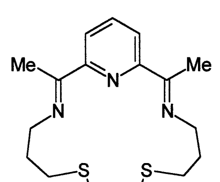
Fig. 6 The structure of $[CuL]BPh_4{\cdot}(CH_3)_2CO$ (**1**·acetone) with ellipsoids of 20% probability. Selected bond lengths (Å) and angles (°): Cu1–N1 1.965(5), Cu1–N8 2.094(5), Cu1–N13 2.077(4), Cu1–N20 1.987(4), N1–Cu1–N8 80.0(2), N13–Cu1–N20 79.3(2), N1–Cu1–N20 139.3(2), N1–Cu1–N13 135.8(2), N20–Cu1–N8 85.9(2), N20–Cu1–N8 130.9(2).

solution of **1** in acetone yields single crystals of $[CuL]BPh_4{\cdot}(CH_3)_2CO$, the acetone solvate of **1**, which slowly loses the solvent molecule. By the X-ray crystallographic study, $[CuL]BPh_4{\cdot}(CH_3)_2CO$ (**1**·acetone) is found to consist of discrete $[CuL]^+$ cations, BPh_4^- anions and acetone solvent molecules (Fig. 6).[13] Thus one may conclude that the reversibility of couple (5) in dichloromethane depends on the nature (possibly shape and size) of the cation. This is presumably due to ion pair formation in CH_2Cl_2 caused by the low value of ε (8.92 at 25 °C).[6] Though interactions in ion pairs are largely electrostatic in nature, specific interactions are possible.[10,14–16] For $[CuL]BPh_4$, ion pair formation in CH_2Cl_2 may be facilitated by aromatic ring stacking.

In this context, a knowledge of the ion pair association of Bu_4NBPh_4 in solution may be imperative. The association constants (K_a) of Bu_4NBPh_4 in some of the solvents used in the present study are given in Table 2.[17–21] In general, $\log K_a$ of an electrolyte varies inversely with ε. Consequently, it is found that only in dichloromethane (Table 2) is ion pair formation significant. It should be noted that K_a values $\leqslant 10\ mol^{-1}\ dm^3$ have no physical meaning.[22]

Concluding remarks

We have shown that BPh_4^- undergoes a one-electron oxidation [couple (5)] in dichloromethane, a solvent of fairly low dielectric constant. The process, however, is not fully reversible. The oxidation of BPh_4^- in solvents of higher dielectric constant is somewhat complicated as several secondary chemical reactions follow the primary electrode process (5). Though the oxidation of BPh_4^- in such solvents on the cyclic voltammetric time scale appears to still be a one-electron process, coulometry indicates a two-electron process. This is because the intermediate solvato species S–BPh_3 undergoes a disproportionation reaction regenerating BPh_4^- [reaction (8)].



L'

The results clearly demonstrate that in most solvents BPh_4^- is not an innocent anion and may act as a one-electron reductant. Earlier it has been observed by Drew *et al.*[23] that attempts to crystallise $[CuL']BPh_4$ from methanol led to the formation of the tetraphenylborate of the corresponding copper(I) species, $[CuL']BPh_4$. In view of the E_{pa} value of BPh_4^- in methanol (Table 2), it appears as if the potential of the $Cu^{II/I}$ couple of the $CuN_2S_3^{2+}$ chromophore in $[CuL']^{2+}$ is sufficiently high to oxidise BPh_4^-. The E_{pa} values in Table 2 also show that in a solvent like methanol, BPh_4^- can undergo aerial oxidation to produce a phenyl radical and S–BPh_3. Apparently, this is why BPh_4^- may sometimes act as a phenylating agent[24] or may lead to the substitution[25] of a proton by the electron-deficient species BPh_3.

Experimental

General

Sodium perchlorate was purchased from Aldrich, USA. The ligand L was synthesised as reported elsewhere.[26] All solvents used for electrochemical experiments were purified by standard procedures.[27] Cyclic voltammetry and coulometry were performed using an EG&G PARC electrochemical analysis system, model 250/5/0, in conventional three-electrode configurations. An ECDA-Pt02 platinum disk electrode obtained from Con-Serv Enterprises, India, and a planar EG&G PARC G0229 glassy carbon milli electrode were used as the working electrodes in cyclic voltammetry.

Syntheses

Bu_4NBPh_4. This salt was synthesised by modifying a reported procedure[28] in the following manner. $NaBPh_4$ (0.34 g, 1 mmol), dissolved in 10 ml of water, was added to Bu_4NBr (0.322 g, 1 mmol), dissolved in 15 ml of water, with stirring. The resulting white colloid-like solution was stirred for 30 min and left in air overnight. The white precipitate, collected by filtration, was washed thoroughly with 150 ml of water and dried *in vacuo* over fused $CaCl_2$. Yield: 0.38 g (68%).

$[CuL]BPh_4$ (1). L (0.44 g, 1 mmol) and $NaBPh_4$ (1.369 g, 4 mmol), dissolved in 30 ml of acetone, were added to a solution of $[Cu(CH_3CN)_4]ClO_4$ (0.328 g, 1 mmol) in 10 ml of acetone under an N_2 atmosphere at room temperature. The resulting deep red reaction mixture was stirred for 2 h. A shiny dark red compound precipitated, which was collected by filtration, washed with 5 ml of acetone and dried *in vacuo* over fused $CaCl_2$. The compound was recrystallised from an acetone–hexane (1 : 2) mixture. Yield: 0.54 g (70%). Anal. found (calcd): C, 75.52 (75.48); H, 5.30 (5.36); N, 10.10 (10.16%). UV/VIS (CH_2Cl_2) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 230 (49 600), 255sh (41 000), 288 (37 200), 425 (8 800).

X-Ray crystallography

The data on **1**·acetone were collected with Mo-Kα radiation using the MARresearch Image Plate System at 293(2) K. The crystal was positioned at 70 mm from the image plate. One hundred frames were measured at 2° intervals with a counting time of 4 min. Data analysis was carried out with the XDS program.[29] The structures were solved using direct methods with the SHELXS-86 program.[30] The non-hydrogen atoms were refined anisotropically and remaining atoms isotropically. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was carried out using

DIFABS.[31] The structures were refined on F^2 using SHELXL-93[32] to $R_1 = 0.0758$ and $wR_2 = 0.2032$ for 4112 reflections with $I > 2\sigma(I)$.

Crystal data. $C_{55}H_{50}BCuN_6O$ (**1**·acetone): $M_w = 885.36$, triclinic, spacegroup P-1, $a = 10.779(17)$, $b = 13.887(17)$, $c = 16.42(2)$ Å, $\alpha = 87.56(1)°$, $\beta = 80.70(1)°$, $\gamma = 83.01(1)°$, $U = 2408(6)$ Å^3, $Z = 2$, $\mu = 0.498$ mm^{-1}, $D_c = 1.221$ g cm^{-3}, 7997 unique data were collected.

CCDC reference number 179190. See http://www.rsc.org/suppdata/nj/b1/b106356c/ for crystallographic data in CIF or other electronic format.

Acknowledgements

M. G. B. D. thanks EPSRC and University of Reading for funds for the Image Plate System. D. D. thanks the Department of Science and Technology, New Delhi, India, for financial support. Useful advice received from a reviewer is gratefully acknowledged.

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7 When reactions (5) and (6) are considered together, reaction (6) has to be rearranged so that the net reaction is:

$$^{\bullet}BPh_4 + e^- \rightleftharpoons BPh_4^-$$
$$S\text{–}BPh_3 + {}^{\bullet}Ph = {}^{\bullet}BPh_4 + S$$
$$\overline{}$$
$$S\text{–}BPh_3 + {}^{\bullet}Ph + e^- = BPh_4^- + S$$

The total free energy change for the net reaction is then given by $-nFE_{1/2} - \Delta G^0$ where $E_{1/2}$ is the half-wave potential for couple (5) in V, n the number of electrons involved in couple (5), F the faraday constant and ΔG^0 the free energy change for reaction (6).
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13 The metal coordination sphere in $[CuL]^+$ is a very distorted tetrahedron. The void space around the metal atom might allow for further coordination but no significant interactions between the cation and the anion less than the sum of van der Waals radii could be observed. However, the acetone molecule forms a weak hydrogen bond to the hydrogen atom on C3. The anion BPh_4^- is found to have B–C distances of 1.641(7)–1.657(6) Å, C_{ipso}–B–C_{ipso} angles in the range 106.6(4)–111.6(4)° and C–C_{ipso}–C angles of 113.6(4)–114.9(5)°. We have investigated the dimensions of the BPh_4^- anion in the Cambridge Crystallographic Database and found that the anion is susceptible to packing effects and in some cases is significantly distorted from tetrahedral. Thus, from 1625 observations of the anion, the average range of the C–B–C angle (defined as the difference between the maximum and minimum angles) is 7.2°, somewhat greater than that observed in the present structure, but 34 examples have a range from 15–32°. The dimensions in the present structure are consistent with a mean B–C distance of 1.659 Å and a C–C_{ipso}–C angle of 114.7°. The average sum of the three angles at C_{ipso} is 359.8° in our case, confirming the trigonal nature of these atoms.
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