Phosphine displacement reactions by some alkyl-substituted 1,10-phenanthrolines with bis(triphenylphosphine)copper(I)tetrahydroborate

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(Received December 24, 1992)

Abstract

The displacement reactions of various alkyl-substituted 1,10-phenanthrolines with bis(triphenylphosphine)-copper(I)tetrahydroborate [$(Ph_3P)_2Cu(BH_4)$] have been investigated. Two series of products from these displacement reactions: (phen)Cu(BH_4) (series 1) and (phen)(Ph_3P)Cu(BH_4) (series 2) have been identified via their spectroscopic properties. Both series 1 and 2 products contain the bidentate tetrahydroborate (η^2-BH_4) group, while the series 2 products also involve the coordination of triphenylphosphine [PPh_3] to the copper(I) centre. In some instances, both series of products may be observed for the same phenanthroline ligand employed. Some series 1 products in the presence of PPh_3 can be converted to their conjugate series 2 products. Both series of displacement products have been characterised by spectroscopic methods: ^1H, ^{13}C, ^{11}B and ^{31}P NMR and FT-IR.

Introduction

The reported examples of copper(I)tetrahydroborato complexes that have been characterised by structural and spectroscopic methods have included examples of the monodentate tetrahydroborate group such as in $(MePh_2P)_3Cu(BH_4)$ [1] and (triphos)Cu(BH_4) [2] (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane), and the bidentate tetrahydroborate group such as $(Ph_3P)_2Cu(BH_4)$ [3, 4] and $(Cy_3P)_2Cu(BH_4)$ [5] (Cy_3P = tricyclohexylphosphine). Of particular interest to this work are the reported examples of copper(I)tetrahydroborato complexes which contain bidentate nitrogen donor ligands, such as the alkyl-substituted 1,10-phenanthrolines [phens].

The BH_4 group is able to attach itself to a metal centre in any one of four possible modes (types I–IV) for a mononuclear complex. Three of these modes involve covalent bonding and ligation of the BH_4 group through bridging hydrogens in a monodentate (η^1-BH_4), type I; bidentate (η^2-BH_4), type II; or tridentate (η^3-BH_4), type III manner to the metal centre. A type IV structure involves ionic bonding between the anionic BH_4 group and the cationic metal centre. As well as a symmetrical mode of attachment of the BH_4 group, unsymmetrical bonding is known for type II complexes [6]. The unsymmetrical nature of the mode of attachment of the BH_4 group is confirmed by both structural (bond angles and bond lengths) and spectroscopic methods, in particular, IR spectroscopy where the peaks associated with the bridging hydrogens exhibit both a weaker intensity and a shift to lower frequency. Thus, IR spectroscopy provides a valuable tool for determining the mode of attachment of the BH_4 group and helps elucidate the complete structure of copper(I)-tetrahydroborato complexes, and indeed other metal tetrahydroborates [7, 8]. Pertinent information to be deciphered from the IR spectrum of a metal tetrahydroborate can include the position and number of peaks corresponding to the number of both the terminal and bridging hydrogens of the BH_4 group. Each structural type has characteristic IR peaks, the location and number of which is slightly different for each of the different bonding modes. The BH_4^- ion is isoelectronic with CH_4, thus the mode of attachment of the tetrahydroborate species to metals is relevant to the catalytic activation of saturated hydrocarbons.

Different types of products have been reported for the displacement reaction with $(Ph_3P)_2Cu(BH_4)$ depending on the particular phen ligand employed, either of the type (phen)Cu(BH_4) (where phen = 2,9-dpm [9] or 2,9-dm-4,7-dpp [6]) or the type (phen)(Ph_3P)Cu(BH_4) (where phen = 1,10-phen [6, 10] or 3,4,7,8-tmp [10]). Ligand abbreviations are given below.

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0020-1693/93/$6.00

The preparation of products of the type (phen)-$Cu(BH_4)$ involves the displacement of two mole equivalents of the unidentate PPh_3 ligand, whereas for products of the type (phen)$(Ph_3P)Cu(BH_4)$ it involves the displacement of only one equivalent of PPh_3 from the original copper(I) centre of $(Ph_3P)_2Cu(BH_4)$ by the bidentate phen ligand employed. Compounds of both types have previously been characterised and shown by spectroscopic and structural methods to contain the bidentate tetrahydroborate group, e.g. (1,10-phen)-$(Ph_3P)Cu(\eta^2\text{-}BH_4)$ [6] and (2,9-dmp)$Cu(\eta^2\text{-}BH_4)$ [9].

With these previous results in mind, this work investigated the displacement reaction between other phen ligands and $(Ph_3P)_2Cu(BH_4)$ to ascertain whether similar displacement products to those already described might also be observed.

Experimental

Materials

The phen ligands were prepared by modifications and/or applications of known literature methods [11–17]. Phen abbreviations are: 1,10-phen = 1,10-phenanthroline; 2-mp = 2-methyl-1,10-phenanthroline (similarly for 4-mp and 5-mp); 2,9-dmp = 2,9-dimethyl-1,10-phenanthroline (similarly for 4,7-dmp, 5,6-dmp and 3,4-dmp); 3,4,7,8-tmp = 3,4,7,8-tetramethyl-1,10-phenanthroline; 2,9-dm-4,7-dpp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. $(Ph_3P)_2Cu(BH_4)$ was prepared from $(Ph_3P)_2Cu(NO_3)$ and $NaBH_4$ [18], while $(Ph_3P)_2Cu$-(BD_4) was prepared using $NaBD_4$ instead of $NaBH_4$. Solvents were distilled, dried and dinitrogen purged before use.

General techniques

IR spectra were recorded as solid samples mixed with KBr (1:10) by diffuse reflectance or from solutions in a 0.3 mm pathlength sealed solution cell (NaCl windows) using a Perkin-Elmer 1720X fourier transform spectrometer. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Microanalyses (C, H, N, P) were performed by the Microanalytical Service of the Chemistry Dept., University of Otago, Dunedin, New Zealand. ^1H, ^{13}C, ^{11}B and ^{31}P NMR spectra were acquired on a Bruker AM300 multinuclear spectrometer. Because of the inherent decomposition problems associated with solutions of ‘unstabilised’ tetrahydroborato complexes, solutions for NMR were prepared immediately before use from dry, dinitrogen-degassed deuterated solvents and stored (if required) in a dinitrogen purged desiccator over P_2O_5.

Preparation of (phen)Cu(BH$_4$) series 1 complexes

Compounds **1**, **2**, **5** and **7** (see Table 1) were prepared by the following general method. To a solution of $(Ph_3P)_2Cu(BH_4)$ (0.92 g, 1.53 mmol) in 300 ml toluene was added the appropriate phen (1.65 mmol) in 120 ml toluene over a period of 30 min at room temperature. The resulting orange solution was stirred for a further 30 min. The crude product (orange ppt.) was collected, recrystallised from CH_2Cl_2 by the slow addition of toluene to yield yellow–orange crystals, and washed with successive portions (3×1 ml) of toluene.

Preparation of (phen)(Ph$_3$P)Cu(BH$_4$) series 2 complexes

Compounds **2**, **4**, **6**. **8**, **9**, **10** and **11** were prepared by the following general methods.

Method A. Compounds **2**, **4**, **6** and **8** were isolated by concentrating the filtrate from the initial preparation of the conjugate series 1 compound on a rotary evaporator to approximately 10 ml and cooling to room temperature. The orange crystals were collected, recrystallised from toluene and washed with successive portions (3×1 ml) of ice-cold toluene.

Method B. Compounds **2**, **4**, **6** and **8** could also be prepared by dissolving the appropriate conjugate series 1 compound (0.35 mmol) in 30 ml toluene and 10 ml CH_2Cl_2, to which was added PPh_3 (0.70 mmol). The mixture was refluxed for 3 h, allowed to cool, filtered and concentrated under a dry nitrogen stream. The pale orange crystals were collected, recrystallised from toluene and washed with successive portions (3×1 ml) of ice-cold toluene.

Combined method. Compounds **9**, **10** and **11** were prepared as for the series 1 compounds, and by method A as for the other series 2 compounds. Both products were shown by melting point, IR and ^1H NMR spectroscopy to be identical.

The corresponding (phen)$Cu(BD_4)$ and (phen)-$(Ph_3P)Cu(BD_4)$ derivatives were prepared by the same methods as described above, starting from $(Ph_3P)_2Cu(BD_4)$.

Results and discussion

It is convenient, with respect to simplifying further discussions to classify each of the two different series of products observed from the displacement reactions of the various phen ligands with $(Ph_3P)_2Cu(BH_4)$. The series 1 displacement products are copper(I)-tetrahydroborato complexes prepared from a displacement reaction involving $(Ph_3P)_2Cu(BH_4)$ and various alkyl-substituted 1,10-phenanthroline ligands, in which the reaction product does not involve coordinated PPh_3 to the copper(I) centre. Similarly, the series 2 dis-

TABLE 1. Characterisation and NMR data for both (phen)Cu(BH_4) and (phen)(Ph_3P)Cu(BH_4) complexes

Complex	Yield[a] (g (%))	m.p. (°C)	Microanalysis	NMR data[b]
(4,7-dmp)Cu(BH_4) (**1**)	0.30 (69)	178	Calc. for $C_{14}H_{16}BN_2Cu$; $M_r = 286.64$ Calc.: C, 58.66; H, 5.63; N, 9.77 Found: C, 58.63; H, 5.66; N, 9.67	^{1}H NMR δ: 0.278, q, $J=80$ Hz, 4H, $-BH_4$; 2.856, s, 6H, 2×$-CH_3$; 7.662, d, $J=4.0$ Hz, 2H, H3(8); 8.152, s, 2H, H5(6); 8.889, s(br), 2H, H2(9). ^{13}C NMR δ: 19.27, 2×$-CH_3$; 123.16; 125.96; 126.18; 128.85; 149.03. ^{11}B NMR δ: −40.32, quintet, $J=81$ Hz, $-BH_4$.
(4,7-dmp)(Ph_3P)Cu(BH_4) (**2**)	A: 0.14 (54) B: 0.12 (63)	154 152	Calc. for $C_{32}H_{31}BN_2PCu$; $M_r = 548.94$ Calc.: C, 70.02; H, 5.69; N, 5.11; P, 5.65 Found: C, 69.96; H, 5.70; N, 5.19; P, 5.62 Found: C, 69.99; H, 5.72; N, 5.16; P, 5.68	^{1}H NMR δ: 0.506, q, $J=80$ Hz, 4H, $-BH_4$; 2.789, s, 6H, 2×$-CH_3$; 7.203–7.356, m, 15H, $-P(C_6H_5)_3$; 7.501, d, $J=4.0$ Hz, 2H, H3(8); 8.085, s, 2H, H5(6); 8.753, s(br), 2H, H2(9). ^{11}B NMR δ: −40.90, quintet, $J=80$ Hz, $-BH_4$. ^{31}P NMR δ: 11.56, s, $-P(C_6H_5)_3$.
(3,4,7,8-tmp)Cu(BH_4) (**3**)	0.11 (22)	181	Calc. for $C_{16}H_{20}BN_2Cu$; $M_r = 314.69$ Calc.: C, 60.95; H, 6.34; N, 8.89 Found: C, 60.87; H, 6.28; N, 8.75	^{1}H NMR δ: 0.287, q, $J=81$ Hz, 4H, $-BH_4$; 2.553, s, 6H, 2×$-CH_3$; 2.725, s, 6H, 2×$-CH_3$; 8.118, s, 2H, H5(6); 8.814, s(br), 2H, H2(9). ^{11}B NMR δ: −42.42, quintet, $J=81$ Hz, $-BH_4$.
(3,4,7,8-tmp)(Ph_3P)Cu(BH_4) (**4**)	A: 0.46 (64) B: 0.13 (76)	153 151	Calc. for $C_{34}H_{35}BN_2PCu$; $M_r = 576.99$ Calc.: C, 70.77; H, 6.11; N, 4.86; P, 5.36 Found: C, 70.67; H, 6.08; N, 4.92; P, 5.27	^{1}H NMR δ: 0.474, q, $J=80$ Hz, 4H, $-BH_4$; 2.433, s, 6H, 2×$-CH_3$; 2.685, s, 6H, 2×$-CH_3$; 7.215–7.368, m, 15H, $-P(C_6H_5)_3$; 8.107, s, 2H, H5(6); 8.568, s(br), 2H, H2(9). ^{13}C NMR δ: 14.88, 2×$-CH_3$; 17.72, 2×$-CH_3$; 122.94; 127.66; 128.83; 128.90; 130.07; 133.03; 133.77; 133.96; 142.63; 143.88; 150.85. ^{11}B NMR δ: −41.38, quintet, $J=80$ Hz, $-BH_4$. ^{31}P NMR δ: 11.20, s, $-P(C_6H_5)_3$.
(5,6-dmp)Cu(BH_4) (**5**)	0.26 (57)	170	Calc. for $C_{14}H_{16}BN_2Cu$; $M_r = 286.64$ Calc.: C, 58.66; H, 5.63; N, 9.77 Found: C, 58.59; H, 5.67; N, 9.72	^{1}H NMR δ: 0.313, q, $J=81$ Hz, 4H, $-BH_4$; 2.804, s, 6H, 2×$-CH_3$; 7.868, s(br), 2H, H3(8); 8.671, d, $J=7.5$ Hz, 2H, H4(7); 8.968, s(br), 2H, H2(9). ^{11}B NMR δ: −42.24, quintet, $J=81$ Hz, $-BH_4$.
(5,6-dmp)(Ph_3P)Cu(BH_4) (**6**)	A: 0.21 (56) B: 0.10 (50)	140 139	Calc. for $C_{32}H_{31}BN_2PCu$; $M_r = 548.94$ Calc.: C, 70.02; H, 5.69; N, 5.11; P, 5.65 Found: C, 70.12; H, 5.73; N, 5.06; P, 5.70	^{1}H NMR δ: 0.520, q, $J=81$ Hz, 4H, $-BH_4$; 2.718, s, 6H, 2×$-CH_3$; 7.192–7.307, m, 15H, $-P(C_6H_5)_3$; 7.737, s(br), 2H, H3(8); 8.528, d, $J=8.0$ Hz, 2H, H4(7); 8.929, s(br), 2H, H2(9). ^{11}B NMR δ: −42.04, quintet, $J=81$ Hz, $-BH_4$. ^{31}P NMR δ: 9.88, s, $-P(C_6H_5)_3$.
(3,4-dmp)Cu(BH_4) (**7**)	0.30 (66)	172	Calc. for $C_{14}H_{16}BN_2Cu$; $M_r = 286.64$ Calc.: C, 58.66; H, 5.63; N, 9.77 Found: C, 58.58; H, 5.68; N, 9.74	^{1}H NMR δ: 0.314, q, $J=81$ Hz, 4H, $-BH_4$; 2.575, s, 3H, $-CH_3$; 2.753, s, 3H, $-CH_3$; 7.830, s(br), 1H, H8; 7.985, d, $J=5.4$ Hz, 1H, H5; 8.204, d, $J=5.8$ Hz, 1H, H6; 8.475, d, $J=6.8$ Hz, 1H, H7; 8.826, s(br), 1H, H2; 9.004, s(br), 1H, H9. ^{11}B NMR δ: −42.28, quintet, $J=81$ Hz, $-BH_4$.
(3,4-dmp)(Ph_3P)Cu(BH_4) (**8**)	A: 0.15 (50) B: 0.13 (66)	143 141	Calc. for $C_{32}H_{31}BN_2PCu$; $M_r = 548.94$ Calc.: C, 70.02; H, 5.69; N, 5.11; P, 5.65 Found: C, 70.08; H, 5.74; N, 5.15; P, 5.60	^{1}H NMR δ: 0.503, q, $J=80$ Hz, 4H, $-BH_4$; 2.473, s, 3H, $-CH_3$; 2.689, s, 3H, $-CH_3$; 7.186–7.322, m, 15H, $-P(C_6H_5)_3$; 7.674, s, 1H, H8; 7.884, d, $J=9.1$ Hz, 1H, H5; 8.109, d, $J=9.1$ Hz, 1H, H6; 8.342, d, $J=8.0$ Hz, 1H, H7; 8.705, s(br), 1H, H2; 8.957, s(br), 1H, H9. ^{11}B NMR δ: −41.94, quintet, $J=80$ Hz, $-BH_4$. ^{31}P NMR δ: 9.81, s, $-P(C_6H_5)_3$.
(2-mp)(Ph_3P)Cu(BH_4) (**9**)	0.61 (72)	134	Calc. for $C_{31}H_{29}BN_2PCu$; $M_r = 534.91$ Calc.: C, 69.60; H, 5.47; N, 5.24; P, 5.79 Found: C, 69.66; H, 5.50; N, 5.14; P, 5.86	^{1}H NMR δ: 0.594, q, $J=81$ Hz, 4H, $-BH_4$; 2.858, s, 3H, $-CH_3$; 7.201–7.330, m, 15H, $-P(C_6H_5)_3$; 7.601, d, $J=8.4$ Hz, 1H, H3; 7.711, dd, J(H8, H9)$=4.9$ Hz, J(H8, H7)$=8.1$ Hz, 1H, H8; 7.857, AB, $J=8.8$ Hz, 2H, H5(6); 8.273, $J=8.2$ Hz, 1H, H4; 8.365, d, $J=8.2$ Hz, 1H, H7; 9.020, s(br), 1H, H9. ^{11}B NMR δ: −41.57, quintet, $J=81$ Hz, $-BH_4$. ^{31}P NMR δ: 9.75, s, $-P(C_6H_5)_3$.

(continued)

TABLE 1. (*continued*)

Complex	Yield[a] (g (%))	m.p. (°C)	Microanalysis	NMR data[b]
(4-mp)(Ph$_3$P)Cu(BH$_4$) (**10**)	0.74 (87)	143	Calc. for $C_{31}H_{29}BN_2PCu$; $M_r = 534.91$ Calc.: C, 69.60; H, 5.47; N, 5.24; P, 5.79 Found: C, 69.68; H, 5.52; N, 5.18; P, 5.83	^{1}H NMR δ: 0.523, q, $J = 82$ Hz, 4H, –BH$_4$; 2.789, s, 3H, –CH$_3$; 7.197–7.310, m, 15H, –P(C$_6$H$_5$)$_3$; 7.530, d, $J = 4.5$ Hz, 1H, H3; 7.675, dd, J(H8, H9) = 4.6 Hz, J(H8, H7) = 8.0 Hz, 1H, H8; 7.896, d, $J = 9.1$ Hz, 1H, H6; 8.053, d, $J = 9.1$ Hz, 1H, H5; 8.348, d, $J = 7.9$ Hz, 1H, H7; 8.840, s(br), 1H, H2; 8.957, s(br), 1H, H9. ^{11}B NMR δ: -41.76, quintet, $J = 81$ Hz, –BH$_4$. ^{31}P NMR δ: 9.92, s, –P(C$_6$H$_5$)$_3$.
(5-mp)(Ph$_3$P)Cu(BH$_4$) (**11**)	0.55 (65)	135	Calc. for $C_{31}H_{29}BN_2PCu$; $M_r = 534.91$ Calc.: C, 69.60; H, 5.47; N, 5.24; P, 5.79 Found: C, 69.64; H, 5.54; N, 5.16; P, 5.85	^{1}H NMR δ: 0.535, q, $J = 82$ Hz, 4H, –BH$_4$; 2.776, s, 3H, –CH$_3$; 7.136–7.341, m, 15H, –P(C$_6$H$_5$)$_3$; 7.680, s(br), 1H, H8; 7.702, s, 1H, H6; 7.755, s(br), 1H, H3; 8.272, d, $J = 8.0$ Hz, 1H, H7; 8.488, d, $J = 8.0$ Hz, 1H, H4; 8.984, s(br), 2H, H2(9). ^{11}B NMR δ: -41.96, quintet, $J = 80$ Hz, –BH$_4$. ^{31}P NMR δ: 9.79, s, –P(C$_6$H$_5$)$_3$.

[a] Where A and B refer to methods A and B, respectively (see 'Experimental'). [b] External references were: boron trifluoride etherate for ^{11}B and 1,2-bis(diphenylphosphino)ethane for ^{31}P.

placement products are complexes in which the reaction product retains PPh_3 coordinated to the copper(I) centre.

Dual products

The displacement reactions involving some phen ligands (4,7-dmp, 3,4,7,8-tmp, 5,6-dmp and 3,4-dmp) have been found in this work to result in the isolation of both a separate series 1 and a series 2 product, which have different physical and chemical properties. The series 1 products are collected as insoluble precipitates when the solvent employed in the displacement reaction is toluene. The conjugate series 2 product is collected by concentrating the filtrate after the initial series 1 displacement product has been collected. The IR spectra of the two different series of products exhibit various differences, aside from the peaks associated with the BH_4 group (to be discussed later), the series 2 products exhibited characteristic peaks indicating the presence of coordinated PPh_3 in the product (ν (cm^{-1}): 500s, 680s, 740s, 1085s, 1430s, 1470s). The IR spectra of the series 1 products did not contain any such peaks. This observation, of two different products obtained from the one reaction for the same phen ligand employed, has not been reported previously.

Single product

The phen ligands 2-mp, 4-mp and 5-mp yield only a series 2 product. This is an interesting observation, when compared to the 'dual' results reported here for the phen ligands 4,7-dmp, 5,6-dmp, 3,4-dmp and 3,4,7,8-tmp. With 2-mp substituted at only the 2-position, it is perhaps not surprising that the only product observed is a series 2 product and not a series 1 product, as has been previously reported for the reactions involving 2,9-dmp [9] and 2,9-dm-4,7-dpp [6]. This observation might be explained when we consider the steric hindrance of 2-mp compared to that of 2,9-dmp and 2,9-dm-4,7-dpp around the copper coordination centre. The two methyl groups at the 2,9-positions of both 2,9-dmp and 2,9-dm-4,7-dpp can be described as a 'closed double gate', effectively blocking the re-entry of PPh_3 ligand to the coordination sphere of the copper(I) centre. With 2-mp substituted at only the 2-position, the ligand can be described as having 'one open-one closed gate', which must in this instance enable significant access for the 'bulky' PPh_3 to the coordination sphere of the copper(I) centre. Efforts to isolate the series 1 products with any of the phen ligands 2-mp, 4-mp or 5-mp proved unsuccessful.

It is only the substitution at both the 2- and 9-positions of the phen ligands so far reported that has been found to be effective in sterically hindering the coordination of PPh_3. The substitutions employed so far at the other positions of the phen ligands are presumably not large enough or orientated in such a manner as to effectively block the coordination of the PPh_3 molecule to the copper(I) centre. From the observations reported here, only 2,9-dmp is effective in producing just a series 1 product. (The preparation and characterisation of (2,9-dm-4,7-dpp)Cu(BH_4) was not reinvestigated as part of this work.) Attempts to isolate a series 2 product for 2,9-dmp, as is observed for the other phen ligands, by both methods reported here were unsuccessful. In each instance, the series 1 complex (2,9-dmp)Cu(BH_4) was reclaimed from the reaction mixture.

What is not so clear, however, is why the phen ligands 4-mp and 5-mp, also result in only a series 2 product, while the corresponding dimethyl-phens (4,7-dmp and 5,6-dmp) result in both a series 1 and series 2 product under the same reaction conditions. This is not to say however, that the series 1 products are not initially prepared and then undergo subsequent conversion *in situ* to the series 2 products, but rather, on the time scale of the experimental conditions used, only the series 2 products for these particular phen ligands could be isolated.

Attempts to isolate a series 1 compound from the displacement reaction employing 1,10-phen proved unsuccessful. In this instance, both the initial precipitate collected and the product obtained from concentrating the filtrate, were shown by spectroscopic evidence to be (1,10-phen)(Ph_3P)Cu(BH_4). The behaviour of 1,10-phen is similar to that reported here for 2-mp, 4-mp and 5-mp.

Conversion of series 1 to series 2 displacement products

The series 2 products **2**, **4**, **6**, **8** can also be prepared by method B (see 'Experimental'). In this case, the appropriate series 1 product is gently refluxed in a 3:1 mixture of toluene:dichloromethane along with a two mole equivalent of PPh_3. The excess of PPh_3 prevents thermal decomposition of both the initial series 1 complex and the final series 2 complex. After 3 h the reaction mixture is allowed to cool and is then concentrated under a dry dinitrogen stream to yield the desired crystalline series 2 product. Alternatively, if the reaction mixture is not heated but allowed to stir overnight at room temperature, a one mole equivalence of PPh_3 will suffice.

As might be expected, if the initial preparation of the series 1 products (**1**, **3**, **5**, **7**) is performed in either a dichloromethane:toluene mixture or just dichloromethane, then only a series 2 product is observed. Presumably, any series 1 product initially formed is converted *in situ* to the series 2 product. The choice of solvent/s, can be used to advantage in preparing particular products when working with any of these particular phen ligands.

The mode of attachment of the BH_4 group reported here in both the series 1 and series 2 products (**1**–**13**) can be examined by IR spectroscopy. It might be expected that the mode of attachment of the BH_4 group in both series of products would be bidentate, as is the case in the (phen)copper(I)tetrahydroborato complexes already reported [6, 9, 10], but the presence of very bulky bidentate ligands could induce a system containing a η^1-BH_4 group. The IR information for the BH_4 group in both (2,9-dmp)Cu(BH_4) and (1,10-phen)(Ph_3P)Cu(BH_4), re-investigated and reported here (see Table 2), agree favourably with the previous IR data reported and indicate a bidentate mode of attachment of the BH_4 group.

The IR spectra of the two conjugate products (5,6-dmp)Cu(BH_4) and (5,6-dmp)(Ph_3P)Cu(BH_4) are shown in Fig. 1. As well as the differences in the ν(B–H_t) and ν(B–H_b) regions, peaks indicating the coordination of PPh_3 in the series 2 product are apparent. The IR data of the BH_4/BD_4 group for the series 1 and series 2 products are presented in Table 2.

An important method for differentiating the bonding modes of the BH_4 group is through the location of the peaks associated with the terminal deformation mode of the BH_3 group (δ(BH_3)) associated with a type I structure, the terminal deformation of the BH_2 group (δ(BH_2)) of a type II structure and the bridge deformation of the BH_3 group (δ(HBH)) associated with a type III structure.

From the IR data in Table 2, it may be readily observed that both the series 1 and series 2 products exhibit δ(BH_2) at approximately 1125 cm^{-1}, which is indicative of the bidentate bonding mode of the BH_4 group. However, further clear IR evidence to support the bidentate mode of attachment of the BH_4 group for both the series 1 and series 2 products is not readily apparent from the corresponding IR spectra, due to interference from peaks associated with the other ligands attached to the copper(I) centre. Compared to the previously reported copper(I)tetrahydroborates, the series 1 and especially the series 2 products exhibit a more complicated IR spectrum, which makes the assignment of the mode of attachment of the BH_4 group, on the basis of just the IR information more difficult. The strongest observable peaks of the BH_4 group in the IR spectra of the series 1 products exhibit ν(B–H_t) in the region 2376–2387 cm^{-1}, ν(B–H_b) in the region 1950–1990 cm^{-1} and a peak in the region 1127–1134 cm^{-1} assigned to δ(BH_2); while the series 2 products exhibit ν(B–H_t) in the region 2324–2345 cm^{-1}, ν(B–H_b) in the region 2030–2088 cm^{-1} and δ(BH_2) in the region 1124–1128 cm^{-1}. These IR data agree well with those previously reported for other copper(I)tetrahydroborates containing a η^2-BH_4 group. In the series 1 products, it was not possible to clearly locate the two peaks which could be assigned to the symmetric and asymmetric modes of vibration of both ν(B–H_t) and ν(B–H_b), which would be further indicative of a type II structure of the BH_4 group.

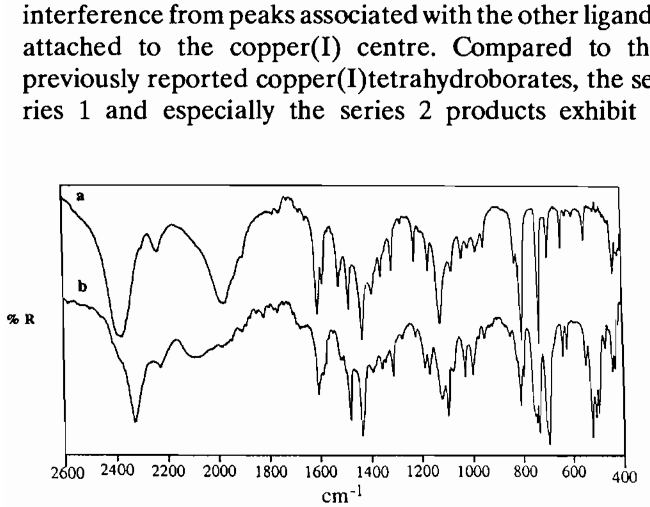

Fig. 1. IR spectra of (5,6-dmp)Cu(BH_4) (a) and (5,6-dmp)(Ph_3P)Cu(BH_4) (b).

The peaks corresponding to both ν(B–H_t) and ν(B–H_b) in the series 2 complexes are less intense when compared to both the other peaks in the same spectra and the corresponding peaks in the conjugate series 1 complexes. This indicates an unsymmetrical mode of attachment of the BH_4 group in the 'confined environment' of these complexes, as has been determined for (1,10-phen)(Ph_3P)Cu(BH_4) by X-ray structure analysis [6].

The technique of isotopic substitution is particularly useful for the series 2 complexes, where the peaks associated with the BH_4 group are often obscured by peaks associated with other ligands bonded to the copper(I) centre. The peaks between 2400 and 2300 cm^{-1} assigned to ν(B–H_t) and especially between 2100 and 1900 cm^{-1} assigned to ν(B–H_b) are often distorted by overtones of the peaks associated with both the PPh_3 and phen ligands present in the complexes. Likewise, the peak at approximately 1125 cm^{-1} assigned to δ(BH_2) is often obscured by the peaks associated with the phen ligand present in the complex. The effect of the distortion is that in many cases the 'fine' structure of the IR peaks associated with both ν(B–H_t) and ν(B–H_b) is obscured, and where evidence of two bridging or two terminal hydrogens is expected, all that is observed is a broad peak, often with an unusual shape.

Further evidence to support the bidentate mode of attachment of the BH_4 group for both the series 1 and series 2 products is provided by the IR spectra of the corresponding tetradeuterioborate complexes (Table 2). The isotopic shift for both series of products was consistently found to be $\nu_H/\nu_D = 1.33$, which is in agreement with that reported elsewhere for similar complexes [10]. Both series of products exhibit two peaks assigned to ν(B–D_t) in the region 1707–1802 cm^{-1}, which is indicative of either a type II or type III structure for the BD_4 group. Unfortunately, the two peaks which

TABLE 2. IR data of the tetrahydroborate/tetradeuterioborate group for both (phen)Cu(BH_4) and (phen)(Ph_3P)Cu(BH_4) complexes

Complex	ν(B–H$_t$)	ν(B–H$_b$)	2×δ(BH_2)	δ(BH_2)	ν(B–D$_t$)	ν(B–D$_b$)	2×δ(BD_2)	δ(BD_2)
(4,7-dmp)Cu(BH/D_4) (**1**)	2376	1978	2234	1128	1790 1736	1490	1676	843sh
(4,7-dmp)(Ph_3P)Cu(BH/D_4) (**2**)	2338	2046	2232	1125	1754 1716	1540	1686	[847]
(3,4,7,8-tmp)Cu(BH/D_4) (**3**)	2378	1968	2232	1130	1795 1737	1480	1678	848
(3,4,7,8-tmp)(Ph_3P)Cu(BH/D_4) (**4**)	2334	2050	2234	1128	1756 1720	1550	1662	841
(5,6-dmp)Cu(BH/D_4) (**5**)	2380	1974 1950	2232	1127	1802 1747	1490	1680	849
(5,6-dmp)(Ph_3P)Cu(BH/D_4) (**6**)	2326 2280sh	2088	2230	1124	1748 1715	1565	1663	846
(3,4-dmp)Cu(BH/D_4) (**7**)	2387	1960	2238	1128	1801 1743	1465	1678	850
(3,4-dmp)(Ph_3P)Cu(BH/D_4) (**8**)	2342 2286sh	2042	2228	1127	1759 1715	[1555]	1667	[847]
(2-mp)(Ph_3P)Cu(BH/D_4) (**9**)	2352	2046	2224	1128	1770 1723	1550	1683	[848]
(4-mp)(Ph_3P)Cu(BH/D_4) (**10**)	2330	2030	2230	1126	1750 1707	1530	1664	[847]
(5-mp)(Ph_3P)Cu(BH/D_4) (**11**)	2324	2058	2225	1122	1748 1715	1550	1665	839
(2,9-dmp)Cu(BH/D_4) (**12**)	2374	1980	2250	1134	1790 1738	[1488]	1686	[853]
(1,10-phen)(Ph_3P)Cu(BH/D_4) (**13**)	2345 2294sh	2058	2226	1126	1767 1723	[1547]	1672	[847]

Data units are cm^{-1}. The modes in brackets were not observed, but calculated from the isotopic shift ratio, sh = shoulder.

might be assigned to ν(B–D$_b$) in the region 1460–1570 cm^{-1}, which would be further indication of a type II structure for both series of products are not clearly identified, due to interference from peaks associated with other ligands attached to the copper(I) centre.

The peak assigned to δ(BH_2) in both series of products undergoes an isotopic shift and is identified in the region 839–850 cm^{-1}. The lack of both an intense peak in the region 1150–1250 cm^{-1} which could be assigned to the bridge deformation of a type III structure, and the corresponding peak in the region 860–940 cm^{-1} for the BD_4 complex, lends further support for the assignment of the η^2-BH_4 group.

With the bidentate mode of the BH_4 group inferred and the bidentate nature of the phen ligand acknowledged, the series 1 products must contain a four-coordinate (with respect to the total number of individual bonds), tetrahedral arrangement of ligands around the copper(I) centre, as has been previously reported for both (2,9-dmp)Cu(BH_4) [9] and (2,9-dm-4,7-dpp)Cu(BH_4) [6], where each of the bridging hydrogens of the BH_4 group occupies a separate tetrahedral site. If the phen ligand employed also acts as a bidentate ligand (as it would be expected to) in the series 2 products, then these complexes must contain a five-coordinate (total number of bonds) tetrahedral arrangement of ligands around the copper(I) centre, as has been previously reported for (1,10-phen)(Ph_3P)Cu(BH_4) [6]. In this instance, both bridging hydrogens of the BH_4 group are orientated in such a manner as to occupy only one tetrahedral site.

The IR data (Table 2) reported here for **4** are different from those reported for the 'same' complex by La Monica *et al.* [10] (ν(B–H$_t$) = 2385; δ(BH_2) = 1095 cm^{-1}), while their corresponding data for the BD_4 complex (ν(B–D$_t$) = 1753, 1710 cm^{-1}) compare favourably. The difference between these IR data for the 'same' complex is difficult to explain, particularly δ(BH_2) = 1095 cm^{-1} as reported by La Monica *et al.* and reported here as δ(BH_2) = 1128 cm^{-1}. The figure reported by La Monica *et al.* is not characteristic of either the bidentate deformation (δ(BH_2) = 1125 cm^{-1}) or of the monodentate deformation (δ(BH_3) = 1060 cm^{-1}) modes that have been previously reported for other copper(I)-tetrahydroborates, but is instead midway between these two values. La Monica *et al.* do not report any values for ν(B–H$_b$), ν(B–D$_b$) or δ(BD_2), even though these assignments were identified in the complexes reported here. The discrepancy between the IR data reported by La Monica *et al.* and those reported here might arise from the different methods of preparation. La Monica *et al.* employed a concentrated stirred suspension of the two reactants and collected the total precipitated product, whereas the method of preparation reported here employed dissolving both the reactants before addition, and resulted in both the initial precipitation of **4**, as well as concentration of the filtrate to yield **5**. Perhaps, under the concentrated reaction conditions employed by La Monica *et al.* a 'mixed' species is observed, having these 'unusual' IR spectral characteristics of the BH_4 group. Indeed, as part of this work before it was realised that there were two separate products for the reaction involving particular phens, the 'combined' products were collected and had different spectroscopic properties than the individual products. In some instances, the initial 'crude' series 1 product shows spectroscopic evidence (IR and ^1H NMR) of the presence of the series 2 product, which is removed by recrystallisation and subsequent washing.

The observation that the displacement reaction of some phen ligands with $(Ph_3P)_2Cu(BH_4)$ results in the isolation of two separate products might explain the anomaly of results that have been reported by different workers using different reaction conditions for the attempted preparation of the same tetrahydroborato complex.

NMR spectroscopy

The ^1H NMR spectrum of **1** exhibits a broad quartet of peaks due to the BH_4 group between $\delta = -0.114$ and 0.696 ppm, with coupling constants $J(H–^{11}B) = 80–82$ Hz. No peaks resembling a septet structure which could be clearly assigned to coupling with ^{10}B were observed in this region for this particular complex. The series of peaks at $\delta = 2.844$, 7.668, 8.108 and 8.854 ppm are assigned to the protons of 4,7-dmp. Spiking a solution of **1** with 4,7-dmp results in a slight chemical shift in the peaks associated with the protons of 'coordinated' 4,7-dmp towards that of 'free' 4,7-dmp. A 10^{-3} M CH_3CN solution of **1** has a conductance of $\Lambda_M = 43.0$ $\mu S\ cm^{-1}$. This indicates the labile nature of the phen ligand, with the resulting possible formation of ionic species of the type $[(phen)Cu]^+[BH_4]^-$ and/or $[(phen)_2Cu]^+[BH_4]^-$ in solution. The absence of any peaks in the region $\delta = 7.0 - 8.0$ ppm, confirms the previous IR characterisation that PPh_3 is absent in this complex. The ^1H NMR spectrum of **2** also exhibits a broad quartet of peaks between $\delta = 0.106$ and 0.908 ppm, assigned to the BH_4 group, where $J(H–^{11}B) = 80$ Hz. This group of peaks is shifted slightly to low-field compared to that observed for **1**. Again, as for **1** no clear septet structure due to coupling with ^{10}B was observed. The series of peaks at $\delta = 2.789$, 7.501, 8.085 and 8.753 ppm are assigned to protons of 4,7-dmp. As for **1**, these peaks in **2** undergo slight chemical shifts compared to the equivalent protons of the 'free' phenanthroline. The spectrum also exhibits a group of peaks between $\delta = 7.203$ and 7.356 ppm, assigned to the protons of PPh_3. The splitting of the peaks due to PPh_3 is evidence of the labile nature of the PPh_3 ligand. Spiking a solution of **2** with excess PPh_3 sees both an increase in intensity of the peaks at about 7.31 ppm and a merging of the PPh_3 peaks, as the complex takes on a more ionic nature in solution. The formation of ionic species in solution again is indicated by conductance measurements. A 10^{-3} M CH_3CN solution of **2** has a conductance of $\Lambda_M = 65.6$ $\mu S\ cm^{-1}$. Ionic species of the type $[(phen)(Ph_3P)_2Cu]^+[BH_4]^-$ and/or $[(phen)(Ph_3P)Cu]^+[BH_4]^-$ are possible.

The ^{31}P NMR spectrum of **2** consists of a single broad peak ($w_{1/2} = 400$ Hz) at $\delta = 11.56$ ppm, assigned to the phosphorus atom of PPh_3. The broad nature of the peak is further evidence of the labile nature of the PPh_3 ligand. Addition of PPh_3 sees the peak sharpen and move towards that of 'free' PPh_3. The ^{31}P NMR spectra for the other series 2 products were similar.

The ^{11}B NMR spectrum of **1** exhibits a symmetrical, well-defined quintet ($w_{1/2} = 230$ Hz) centred at $\delta = -40.32$ ppm in the expected ratio 1:4:6:4:1, with $J(^{11}B–H)$ values of 80 to 82 Hz, similar values to that observed for **1** by ^1H NMR. Similarly, the ^{11}B NMR spectrum of the conjugate series 2 product **2** exhibits a symmetrical, well-defined quintet ($w_{1/2} = 250$ Hz) centred at $\delta = -40.90$ ppm with $J(^{11}B–H)$ values of 79 to 81 Hz, similar to values observed by ^1H NMR for **2**. The ^{11}B NMR spectra for the other members of both the series 1 and series 2 products were similar.

Strength of 'terminal' and 'bridging' bonding of the tetrahydroborate group

The IR data (Table 2) also give an indication of the relevant strength of both $\nu(B–H_t)$ and $\nu(B–H_b)$ of the BH_4 group for both the series 1 and series 2 products and this can be represented graphically (Fig. 2). The individual points for the location of $\nu(B–H_t)$ and $\nu(B–H_b)$ for each of the complexes **1–13** in Fig. 2 are the strongest observed peaks in both the $\nu(B–H_t)$ and $\nu(B–H_b)$ regions.

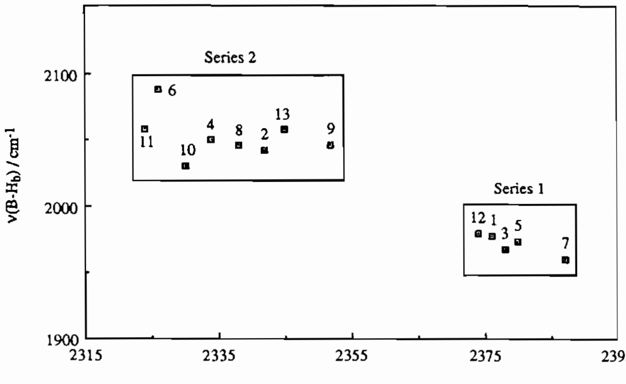

Fig. 2. $\nu(B–H_b)$ vs. $\nu(B–H_t)$ for both $(phen)Cu(BH_4)$ and $(phen)(Ph_3P)Cu(BH_4)$ complexes.

There are two 'clusters' apparent, one corresponding to the series 1 products and the other to the series 2 products. The series 1 products are characterised from Fig. 2 as exhibiting ν(B–H$_b$) at lower energy and ν(B–H$_t$) at higher energy than the series 2 products. This is especially noticeable for those phens where both a series 1 and a conjugate series 2 product are observed.

The strength of bonding of the terminal and bridging hydrogens of the BH_4 group in both the series 1 and series 2 products is important in determining the potential reductive capabilities of these complexes. It has been proposed that the reduction of small heteroallene molecules by similar complexes occurs via insertion of the heteroallene between the metal centre and the boron atom of the BH_4 group [5]. While this is likely in the case of a covalent metal tetrahydroborate, conductance measurements indicate the probable ionic nature of the series 1 and series 2 complexes in solution, and therefore reduction of the heteroallene is more likely to occur via the $[BH_4]^-$ ion [10]. If this is the case, then from the IR data reported here we would expect the heteroallene insertion to be more efficient with the series 1 complexes because of the inherent weaker bonding of the bridging hydrogens in this series.

The NMR and IR data for the previously reported (2,9-dmp)Cu(BH_4) (**12**) and (1,10-phen)(PPh_3)Cu(BH_4) (**13**) complexes have been included for comparison, as each can be considered to be a 'characteristic complex' of each of the two distinct displacement series, because their spectroscopic and structural properties have been previously well documented. The comparison complexes **12** and **13** were prepared by the same method reported here for the preparation of the other (phen)-copper(I)tetrahydroborato complexes (**1–11**). The spectroscopic data reported here for the complexes **12** and **13**, agree well with those reported elsewhere for the same complexes.

From the results reported here, it is apparent that the reaction conditions used for the preparation of a particular complex are important in determining the structural characteristics for that particular complex. If the complex is prepared in toluene at room temperature, then both a series 1 and a series 2 product are possible for some particular phen ligands. However, if the same phen ligand is employed and the reaction is performed in dichloromethane, then only a series 2 product is observed.

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