Journal of

The Chemical Society,

Chemical Communications

NUMBER 5/1977 2 MARCH

$[(MePh_2P)_3CuBH_4]$: a Single M–H Bridged Tetrahydroborate

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Summary The single-hydrogen bridge attachment of BH_4 to copper in $[(MePh_2P)_3CuBH_4]$ is the first reported linkage of that type of BH_4 to copper.

OF the three possible orientations (I)—(III) of the BH_4 group to metals only (II) and (III) have been reported for copper.[1] We now report a complex of type (I).

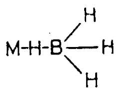
$NaBH_4$ (5 mmol) in ethanol was added to a solution of $[Cu(MePh_2P)_3Cl]$ (4 mmol) in $CHCl_3$ (30 ml). Evaporation to dryness and dissolution in methylene dichloride followed by crystallization with pentane (at −20 °C) resulted in white crystals which were dried under high vacuum. The compound analysed as $C_{39}H_{43}P_3BCu$, m.p. 119—121 °C (decomp. slowly).

The solid-state i.r. spectrum shows bridging and terminal B–H stretching modes. The terminal stretching frequency at 2315 cm^{-1} with a shoulder at slightly higher frequency lies towards the lower end of the frequency range predicted by Mark *et al.* for monodentate borohydride co-ordination.[2] The bridging B–H stretch appears as a sharp singlet at 2050 cm^{-1} with no other peak assignable to the B–H unit in this region; *i.e.*, no splitting into asymmetric and symmetric modes was seen as observed for bidentate attachment.[3] A strong deformation band with a shoulder at higher frequency is also predicted in the range 1000—1150 cm^{-1} for the monodentate attachment. A very strong band at 1060 cm^{-1} (with a possible shoulder at 1075 cm^{-1}) is observed which cannot be ascribed to the phosphine ligands in the complex. The i.r. spectrum of the tetradeuterioborate copper complex supports the above assignments with the predicted doublet resolved in the terminal stretching frequency region (1735 and 1690 cm^{-1}), a strong singlet

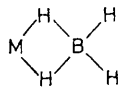
TABLE. I.r. solution data ($CHCl_3$) of $[(Ph_2MeP)_2CuBH_4]$ (Assignments shown based on refs. 2 and 3).

Solution (0·04 g ml^{-1})		Solution (0·7 g ml^{-1})		Solid-state
B–H_t (2400—2600)	2370 sh 2340 vs 2300 sh	B–H_t (2300—2450)	2370 sh 2300 s	2335 sh 2315 vs
Overtone of BH_2 deformation	2240 w		2240 vw (difficult to discern)	
B–H_b (1950—2150)	2010 s	B–H_b (*ca.* 2000)	2035 s	2050 s,br
	1970 sh			
Bridge stretch (1300—1500)	1370 m		1380 vw	
BH_2 deformation (1100—1200)	1125 s		1125 m	
	1060 vw	BH_3 deformation (1000—1150)	1060 s	1060 vs
			1075—1080 sh	1075 sh

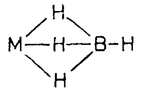
for the bridge stretch at 1510 cm^{-1}, and the deformation mode appearing at 805 cm^{-1}. $\nu_H : \nu_D$ = 1·35 and 1·32, respectively, both values being comparable to values obtained in other deuteriation studies.[2]



(I)



(II)



(III)

That a complex different from the bis complex is observed is illustrated by solution data on dilute (0·04 g ml^{-1}) and concentrated (0·7 g ml^{-1}) samples of the Ph_2MeP complex as shown in the Table. The expected doublets in the terminal and bridging regions are seen for the dilute sample where the phosphine ligands show a higher degree of dissociation and thus the bidentate species is dominant. The very weak absorptions that occur at 2300 and 1060 cm^{-1} are attributed to the presence of a small amount of the monodentate species. This may be justified by comparison with the more highly concentrated sample which clearly shows that the values for absorptions attributed to B–H terminal linkages have decreased as predicted; the doublet in the bridging region no longer exists but has been replaced by the appearance of a singlet, the bridge stretch and bridge deformation absorptions have weakened accordingly, and the peak at 1060 cm^{-1} has become strong. Comparison with solid-state values may also be made from data in the Table. The possibility of the i.r. bands being due to BH_4^- is precluded on the basis of the ^1H n.m.r. spectral data.

The ^1H n.m.r. spectrum of $[(MePh_2P)_3CuBH_4]$ confirms the presence of the phenyl groups (δ 7·3) and methyl group [δ (Me) 1·7, J_{P-H} 4·5 Hz]. The B–H protons appear as a broad singlet [$\delta(CDCl_3)$ + 0·9, Me_4Si standard], which sharpens significantly upon lowering the temperature (−100 °C) thereby indicating effective quadrupole-induced ^{10}B and ^{11}B spin relaxations ('thermal' decoupling). The singlet resonance for the BH_4 hydrogens at −100 °C also suggests a rapid intramolecular exchange process or equivalence of all B–H hydrogens. Such behaviour is consistent with other metal–BH_4 complexes.[4]

Added in proof: It has been suggested (P. Dapporto, S. Midollini, A. Orlandini, and L. Sacconi, *Inorg. Chem.*, **1976**, **15**, 2768) (published after acceptance of this communication), that in $[Cu(P_3)(BH_4)]$ the BH_4 acts as a 'perturbed' bidentate ligand by comparison with an analogous cobalt complex. Although our complex could be considered to bind in the same manner, one must consider the ability of the cobalt, as compared to the copper, to form a distorted square pyramid as well as the question of 'how perturbed must the linkage be to be considered different'. *X*-Ray diffraction studies currently being carried out hopefully will clarify the mode of attachment in the compound reported herein.

We thank the National Science Foundation for a fellowship (J.C.B.) and Research Corporation and Utah State University Division of University Research for financial support.

(*Received*, 28*th September* 1976; *Com.* 1098.)

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[3] Assignments are based on discussion of S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, 1968, **7**, 1051. Other studies include: J. M. Davidson, *Chem. and Ind.*, 1964, 2021; F. Cariati and L. Naldini, *Gazzetta*, 1965, **95**, 3.

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