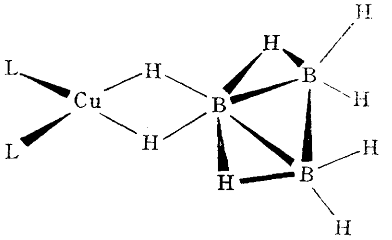
Preparation and Characterization of Octahydrotriboratobis(triphenylphosphine)copper(I)

By STEPHEN J. LIPPARD* and DAVID UCKO

(*Department of Chemistry, Columbia University, New York, N.Y.* 10027)

SEVERAL transition-metal borohydride complexes have recently been synthesized and their structural properties investigated.[1,2] As an extension of our work on various $L_2Cu(BH_4)$ compounds,[2,3] we have studied the corresponding $L_2Cu(B_3H_8)$ system, where L = triarylphosphine. Since it is known from *X*-ray diffraction[2] that $(Ph_3P)_2Cu(BH_4)$ contains a doubly-bridged Cu–BH_4 linkage, we felt the presence of terminal $-BH_2$ groups in the $B_3H_8^-$ ion[4] would make it a likely candidate as a ligand.

From aqueous acetone solutions containing $(Ph_3P)_3CuCl$[1b] and CsB_3H_8, the white crystalline product, octahydrotriboratobis(triphenylphosphine)copper(I), was isolated [m.p. (decomp.) 158—159°].† Infrared spectrum of the complex, mulled in Nujol, revealed three intense bands in the B–H (terminal) stretching frequency region (2495, 2462, 2418 cm.$^{-1}$) and a broad apparent doublet in the B–H (bridging) region (2100–2035 cm.$^{-1}$). Whereas five B–H (terminal) stretching frequencies might be expected for the free $B_3H_8^-$ ion (a broad envelope at $2485 > \bar{\nu} > 2280$ cm.$^{-1}$ was actually observed for CsB_3H_8), the presence of three bands for the complex is consistent with the following proposed structure, in which L represents triphenylphosphine:



The persistence of such a structure in chloroform and benzene solutions of the complex was revealed by infrared spectral comparisons and by conductivity studies, which showed the compound to be a non-electrolyte. Verification of the proposed structure is currently being sought in our laboratories by *X*-ray diffraction.

When $(Ph_3P)_2Cu(B_3H_8)$ was dissolved in acetonitrile and its molar conductivity as a function of concentration measured, plots of Λ_M versus $\sqrt{C}$ had straight-line slopes of 700, which is what would be expected for a 2 : 1 electrolyte in this solvent.[5] This interesting behaviour may be explained by postulating the formation of the trinuclear $[(Ph_3P)_2Cu]_3B_3H_8^{2+}$ ion, in which each BH_2-unit of the $B_3H_8^-$ ion is bonded *via* double hydrogen bridges to a bis(triphenylphosphine)copper(I) moiety. Since various electron-pair donors can open the $B_3H_8^-$ triangle for the free ligand,[6] it is possible that an attack on the triangle of boron atoms in the complex by acetonitrile initiates the dissociation process in that solvent. Solvent attack on the copper atom seems unlikely since we have found $(Ph_3P)_2Cu(BH_4)$ to be a non-conductor in acetonitrile. The oligomerization of the $(Ph_3P)_2Cu(I)$ group by means of $-BH_2$ bridges has previously been reported for μ-borohydridobis[bis(triphenylphosphine)copper(I)]$^+$ salts.[7]

We thank Dr. Frank Klanberg of Du Pont for a generous supply of CsB_3H_8 and the National Science Foundation for financial support.

(*Received, August 4th,* 1967; *Com.* 826.)

---

† Dr. Frank Klanberg of Du Pont has also isolated this complex, as well as other $B_3H_8^-$ transition-metal complexes. (Private communication.)

[1] (a) J. M. Davidson, *Chem. and Ind.*, 1964, 2021; (b) F. Cariati and L. Naldini, *Gazzetta*, 1965, **95**, 3; 1965, **95**, 201; (c) N. F. Curtis, *J. Chem. Soc.*, 1965, 924; (d) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1966, 182; (e) P. H. Bird and M. R. Churchill, *Chem. Comm.*, 1967, 403.

[2] S. J. Lippard and K. M. Melmed, *J. Amer. Chem. Soc.*, 1967, **89**, 3929; *Inorg. Chem.*, 1967, **6**, in the press.

[3] S. J. Lippard and D. Ucko, unpublished work.

[4] C. R. Peters and C. E. Nordman, *J. Amer. Chem. Soc.*, 1960, **82**, 5758.

[5] A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, 1967, **6**, 458.

[6] R. Schaeffer, International Symposium, Boron–Nitrogen Chemistry, quoted in W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, 1963, p. 198.

[7] F. Cariati and L. Naldini, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2243.