(5) J. A. Stritar, Ph.D. Thesis, Stanford University, 1968.
(6) Our measurements were made in a KBr pellet and the value is in satisfactory agreement with that reported by Klein et al. (1316 cm^{-1})[2] and by A. N. Speca, N. M. Karayannis, and L. L. Pytlewski, *J. Inorg. Nucl. Chem.*, **35**, 3113 (1973) (3113 cm^{-1}).
(7) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).
(8) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1, (1968).
(9) M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).
(10) B. Ochiai, "Aromatic Amine Oxides", Elsevier, Amsterdam, 1967, p 97. Here the pK_a for pyridine oxide is quoted as 0.80; that for pyrazine oxide is almost certainly lower.
(11) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).
(12) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

Contribution from the Evans Laboratory of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Comparison of Infrared and Nuclear Magnetic Resonance Solution Spectra of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ with Those of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$

G. G. Outterson Jr., V. T. Brice, and S. G. Shore*

Received October 20, 1975 AIC50753O

Interest in the mode of bonding of Cu(I) to the $B_{10}H_{10}^{2-}$ framework in $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ has recently been rekindled by an x-ray study and the solid-state infrared spectrum of this compound[1] and that of $Cu_2B_{10}H_{10}$.[2] The current results imply Cu–H–B bridge bonding as a significant mode of interaction in the solid state, as well as the previously considered three-center bonding of Cu(I) with a B–B edge of each $B_{10}H_{10}^{2-}$ polyhedron. Since one of the primary pieces of evidence for Cu–H–B bonding is based upon studies of infrared spectra as mulls, it is of interest to determine if the solution infrared spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ also displays a band which can be attributed to Cu–H–B interaction. It is also of interest to determine if the NMR spectra of this compound (^{1}H and ^{11}B) are consistent with a fluxional system. Fluxional character appears to be a property of bis(triphenylphosphine)copper(I) derivatives of borane anions,[3] with the exception of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$ and its methyl derivatives.[4]

In the Nujol mull infrared spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$, broad weak bands between 2150 and 2400 cm^{-1} have been assigned to Cu–H–B bridge stretching modes.[1] Similar bands are also reported for the solid-state spectra of $Cu_2B_{10}H_{10}$ (2100–2300 cm^{-1}),[2a] $[(C_6H_5)_3P]_2CuBH_4$ (2010 cm^{-1}),[5] and $[(C_6H_5)_3P]_2CuB_3H_8$ (2045, 2100 cm^{-1}).[6] Figure 1a shows the Nujol mull spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$. The bands assigned to Cu–H–B stretching modes are of low intensity, comparable to the triphenylphosphine deformations at ca. 1600 cm^{-1}. Figure 1b shows the spectrum of this compound in $CHCl_3$ solution. The intensity of the region assigned to the Cu–H–B bridging bands is markedly enhanced, thus implying Cu–H–B interaction in solution.

The compound 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$ is related to $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ in that the Cu(I) is bound to a boron framework which has only single terminal protons, i.e., no $-BH_2$ groups. The available evidence is consistent with the Cu(I) being bound directly to two basal borons without significant Cu–H–B interaction.[4] The Nujol mull spectrum of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$ has slight absorptions at ca. 2280 and 2325 cm^{-1} (Figure 1c), but these bands are characteristic of the $B_5H_8^-$ anion (see inset to Figure 1c). The solution spectrum of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$ shows little or no evidence for the bands at 2280 and 2325 cm^{-1}. It should be noted that these bands in the solid state and in solution are appreciably weaker, compared to the triphenylphosphine bands, than the Cu–H–B bands in the spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$.

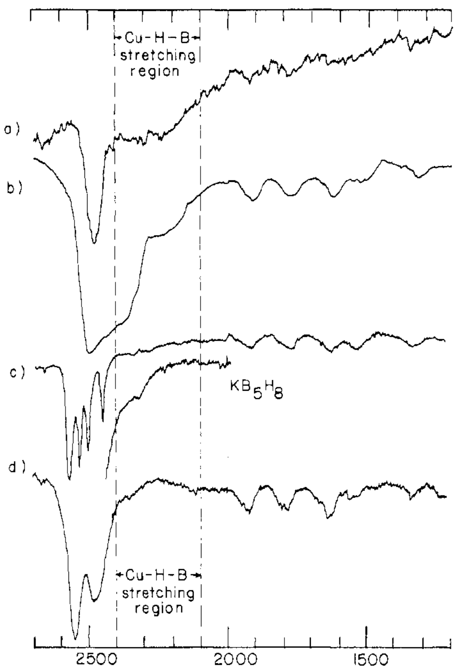
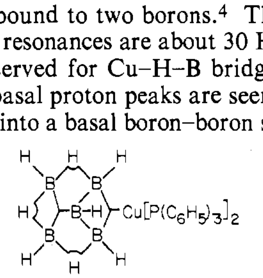


Figure 1. (a) Nujol mull spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$; (b) $CHCl_3$ solution spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$; (c) Nujol mull spectrum of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$; (d) $CHCl_3$ solution spectrum of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$.

The pulsed Fourier transform ^{1}H NMR (90 MHz) spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ was obtained at +30 °C and at −60 °C in $CDCl_3$. The only difference between the two spectra is that, at the lower temperature, the peaks are somewhat sharper. The spectrum consists of a large peak due to the phenyl protons and two peaks due to boron hydride protons. The two peaks have chemical shifts of τ 6.35 and 9.15. These compare to τ 5.7 and 9.1 for $K_2B_{10}H_{10}$.[7] The proton resonances in $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ are severely broadened. The resonance at τ 9.15 (−60 °C) has a half-width of the same order as other Cu–H–B bridged species (100 Hz).[3] The presence of single axial and equatorial resonances is consistent with a fluxional system. While fluxional behavior does not necessarily imply Cu–H–B interaction, this property occurs in other Cu–H–B bridged Cu(I) boranes:[3] $[(C_6H_5)_3P]_2CuBH_4$ and $[(C_6H_5)_3P]_2CuB_3H_8$. The ^{11}B NMR spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ is the same, with respect to chemical shifts, as that of a ^{1}H-decoupled spectrum of $K_2B_{10}H_{10}$[7] except that the peaks are broader.

The fluxional behavior of the B_{10} species contrasts sharply with that of 2,3-μ-$[((C_6H_5)_3P])_2CuB_5H_8$. This salt has a ^{1}H NMR spectrum consistent with a static structure in which the Cu(I) is directly bound to two borons.[4] The half-widths of the basal terminal resonances are about 30 Hz which is much less than that observed for Cu–H–B bridges species. Two distinct terminal basal proton peaks are seen, consistent with insertion of Cu(I) into a basal boron–boron site (see I). This



I

contrasts to the B_{10} species where there is only one peak due to the terminal equatorial protons.

Experimental Section

Reagents. $(NH_4)_2B_{10}H_{10}$[7] and $[(C_6H_5)_3P]_3CuCl$[5] were prepared according to the literature. $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ was prepared by the method of Gill and Lippard[1] from the above reactants. Preparation of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$[4] has been described previously. Anal. Calcd for 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$: C, 66.5; H, 5.85; B, 8.30; P, 9.55; Cu, 9.80. Found: C, 66.95; H, 6.00; B, 7.95; P, 9.30; Cu, 9.70. Calcd for $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$ (Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.): C, 62.06; H, 5.06; B, 7.65; P, 8.76. Found: C, 61.82; H, 5.41; B, 7.63; P, 9.02.

Spectra. The ^1H NMR spectra were obtained at 90 MHz with a Bruker HX-90 NMR spectrometer. Proton chemical shifts are relative to $Si(CH_3)_4$, τ 10.00 ($CHCl_3$, τ 2.75). Infrared spectra were obtained with a Perkin-Elmer 457 infrared spectrometer. The solution infrared spectrum of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$ was recorded using a cell path length of 0.1 mm. The solution infrared spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ was recorded using custom-built matched cells with a path length of 8 mm. The cells are sufficiently matched that $CHCl_3$ absorptions are canceled out. The cells are of stainless steel with KBr windows.

Acknowledgment. We wish to thank the National Science Foundation for support of this work.

Registry No. 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$, 32491-36-4; $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$, 54020-26-7.

References and Notes

(1) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975).
(2) (a) T. E. Paxton, M. F. Hawthorne, L. D. Brown, and W. N. Lipscomb, *Inorg. Chem.*, **13**, 2772 (1974); (b) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962); (c) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **48**, 729 (1962).
(3) (a) C. H. Bushweller, H. Beall, M. Grace, W. J. Dewkett, and H. S. Bilofsky, *J. Am. Chem. Soc.*, **93**, 2145 (1971), and references therein; (b) H. Beall and C. H. Bushweller, *Chem. Rev.*, **73**, 465 (1973).
(4) (a) V. T. Brice and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 344 (1975). (b) This structure has been recently established by a single crystal x-ray study (N. N. Greenwood, personal communication).
(5) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).
(6) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1050 (1968).
(7) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

Contribution from the W. R. Kenan, Jr. Laboratory,
Department of Chemistry, The University of North Carolina,
Chapel Hill, North Carolina 27514

Effect of Solvent on the Energy of Intervalence-Transfer Bands

M. J. Powers, R. W. Callahan, D. J. Salmon,
and Thomas J. Meyer*

Received October 28, 1975 AIC50777V

Mixed-valence compounds often have unusual absorption bands in their electronic spectra.[1] In systems where metal–metal interactions are sufficiently strong, the metal sites are equivalent and the absorption bands have their origin in transitions involving delocalized molecular orbitals over the various metal centers.[1-3] If metal–metal interactions are relatively weak, the metal sites are nonequivalent and localized valences are present. In this latter class of compounds, there commonly appear low-energy absorption bands which can be assigned to intervalence-transfer (IT) transitions.[4,5] In IT transitions, light-induced electron transfer occurs between different valence state sites (eq 1).

$$[\mathrm{M(III)}\text{-}\mathrm{M(II)}] \xrightarrow{h\nu} [\mathrm{M(II)}\text{-}\mathrm{M(III)}]^* \tag{1}$$

Hush has developed a treatment which predicts the properties of IT bands in cases where delocalization is not extensive. One of the predictions made is that the energies of IT bands should depend on solvent dielectric properties. This prediction has been borne out for the symmetrical mixed-valence ions $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$ [6] (4,4'-bpy is 4,4'-bipyridine) and $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+}$ [7] (bpy is 2,2'-bipyridine; pyr is pyrazine). In contrast, the energy of the IT band in the Creutz and Taube ion $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{5+}$ does not vary with solvent,[8] apparently because of extensive delocalization.[7]

In earlier papers the mixed-valence properties of a series of unsymmetrical dimers were reported.[9] In the ion $[(NH_3)_5Ru(pyr)RuCl(bpy)_2]^{4+}$, there is an oxidation-state asymmetry induced by the difference in coordination environments, and the Ru(III) site is localized on the pentaammine end.[9] The IT solvent dependence is more difficult to test experimentally for unsymmetrical cases and insufficient data were available in the earlier work to make a searching test. Because of the importance of establishing the validity and limitations of the Hush treatment, of relating IT processes to thermal electron-transfer processes in solution, and of probing the effects of electronic delocalization on mixed-valence properties, we have carried out a detailed study of the variation of IT band with solvent for the ion $[(NH_3)_5Ru(pyr)RuCl(bpy)_2]^{4+}$.

Experimental Section

Measurements. Ultraviolet–visible and near-infrared spectra were recorded using Cary Models 14 and 17 and Bausch and Lomb 210 spectrophotometers. Electrochemical measurements were vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2 °C and are uncorrected for junction potentials. The measurements were made using a PAR Model 173 potentiostat for potential control with a PAR Model 175 universal programmer as a sweep generator for voltammetric experiments.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques.[9] Acetonitrile (MCB Spectrograde) was dried over Davidson 4-Å molecular sieves for electrochemical measurements and used without drying for spectral measurements. Water was deionized and then distilled from alkaline permanganate. Propylene carbonate was vacuum distilled with the middle 60% collected. Dimethyformamide (reagent grade) was stirred over molecular sieves (type 3A pellets) for 24 h and then vacuum distilled from phosphorus pentoxide. All other solvents (reagent grade) were used without further purification. The preparations of the complexes $[(NH_3)_5Ru(pyr)RuCl(bpy)_2]^{4+/3+}$ [9] and $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+/2+}$ [7] have been reported elsewhere.

Results

Electrochemical data and IT absorption band maxima are given in Table I. The $E_{1/2}$ values are from voltammetry and cyclic voltammetry. The slopes of plots of E vs. log $[i/(i_1 - i)]$ from voltammetry and the difference between anodic and cathodic peak potentials (ΔE_p) gave values between 60 and 100 mV. The cyclic voltammograms were essentially invariant to changes in the sweep rate in the range 50–500 mV/s, and the higher than theoretically predicted ΔE_p values apparently arise from uncompensated solution resistance.

Except for the usually small correction term for differences in diffusion coefficients, the $E_{1/2}$ values are reduction potentials for the couples

$$\begin{aligned}&[(bpy)_2ClRu^{III}(pyr)Ru^{III}C(bpy)_2]^{4+} + e^- \\ &\quad \rightarrow [(bpy)_2ClRu^{III}(pyr)Ru^{II}Cl(bpy)_2]^{3+} \quad (E_{1/2}(2))\end{aligned} \tag{2}$$

$$\begin{aligned}&[(bpy)_2ClRu^{III}(pyr)Ru^{II}Cl(bpy)_2]^{3+} + e^- \\ &\quad \rightarrow [(bpy)_2ClRu^{II}(pyr)Ru^{II}Cl(bpy)_2]^{2+} \quad (E_{1/2}(1))\end{aligned} \tag{3}$$

and

$$\begin{aligned}&[(NH_3)_5Ru^{III}(pyr)Ru^{III}Cl(bpy)_2]^{5+} + e^- \\ &\quad \rightarrow [(NH_3)_5Ru^{III}(pyr)Ru^{II}Cl(bpy)_2]^{4+} \quad (E_{1/2}(2))\end{aligned} \tag{4}$$

$$\begin{aligned}&[(NH_3)_5Ru^{III}(pyr)Ru^{II}Cl(bpy)_2]^{4+} + e^- \\ &\quad \xrightarrow[\mathcal{E}_1^{\circ\prime}]{} [(NH_3)_5Ru^{II}(pyr)Ru^{II}Cl(bpy)_2]^{3+} \quad (E_{1/2}(1))\end{aligned} \tag{5}$$