$$a_{11} = -k_{1f}\left(\frac{\mathrm{Cu}}{A} + \mathrm{HL}\right) - k_{1r}\left(\frac{1}{B}\right)$$

$$a_{12} = k_{1f}\left(\frac{\mathrm{Cu}}{C}\right) - k_{1r}\left(\frac{1}{D}\right)$$

$$a_{21} = k_{2f}\left(\frac{\mathrm{CuHL}}{A} - \frac{\mathrm{HL}}{B}\right)$$

$$a_{22} = -k_{2f}\left(\frac{\mathrm{CuHL}}{C} + \frac{\mathrm{HL}}{D}\right) - k_{2r}$$

where $K_p = (K_1 \cdot K_{a3})/K_3$ and

$$A = \mathrm{NUM}/[\mathrm{H}(K_{a2} + \mathrm{HL})\mathrm{H} + \mathrm{H}(K_{a2} + 2\mathrm{HL})K_p + \mathrm{H}K_{a2}(\mathrm{CuL} + \mathrm{L})]$$

$$B = \mathrm{NUM}/[\mathrm{H}(K_{a2} + \mathrm{H} + \mathrm{HL})\mathrm{H} + \mathrm{L}(K_{a2} + 2\mathrm{H})\mathrm{H} + K_{a3}(K_{a2} + 2\mathrm{HL})\mathrm{H} + \mathrm{H}(K_{a2} + 2\mathrm{H})\mathrm{CuL}]$$

$$C = \mathrm{NUM}/[\mathrm{H}(\mathrm{CuL} + \mathrm{L} + \mathrm{H} + K_p)K_{a2} + \mathrm{H}\cdot\mathrm{HL}\cdot\mathrm{H} + 2K_{a2}\cdot\mathrm{L}\cdot K_p]$$

$$D = \mathrm{NUM}/[\mathrm{H}(K_{a2} + \mathrm{H} + \mathrm{HL})\mathrm{H} + \mathrm{L}(K_{a2} + 2\mathrm{H})\mathrm{H} + K_{a3}(K_{a2} + 2\mathrm{HL})\mathrm{H} + \mathrm{CuL}(2K_{a3} + \mathrm{H})K_{a2}]$$

$$\mathrm{NUM} = [\mathrm{H} + K_p]\cdot[\mathrm{H}(K_{a2} + \mathrm{H} + \mathrm{HL}) + \mathrm{L}(K_{a2} + 2\mathrm{H}) + K_{a3}(K_{a2} + 2\mathrm{HL})] + [\mathrm{CuL}(K_{a3} + \mathrm{H})K_{a2} + \mathrm{H}\cdot\mathrm{CuL}\cdot\mathrm{H}]$$

A Cryoscopic Study of Copper(I) Hydride–Phosphine Complexes

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Abstract: Pyridine solutions of copper(I) hydride plus aryl or alkyl phosphines and phosphites have been studied by freezing point depression. Cryoscopic titration curves for the most basic phosphines show a molality minimum which corresponds to the formation of $R_3P(CuH)_2$. It is proposed that association occurs *via* hydride bridges. 1,2-Bis(diphenylphosphino)ethane (diphos) yields a molality minimum corresponding to diphos$(CuH)_2$. Solutions and solid samples of copper hydride–phosphine complexes do not have a high order of thermal stability, and this leads us to question the validity of a previous report on highly stable copper hydride–phosphine complexes.

The preparation of copper hydride was first reported by Würtz in 1844 making it the oldest properly characterized metal hydride.[2] By treating an aqueous solution of copper(II) sulfate with hypophosphorous acid, Würtz obtained a thermally unstable red-brown material of the approximate composition CuH. More recently, Wiberg[3] reported that copper hydride could be prepared by the metathesis of copper(I) iodide and lithium tetrahydroaluminate in a pyridine–ether solvent system. When prepared by this method, copper hydride was reported to be soluble in pyridine, and a pure compound could be obtained on repeated precipitation from this solvent by addition of ether. In contrast, a nondestructive solvent has never been found for the copper hydride prepared by the Würtz method.

The insoluble form of copper hydride has been the topic of much study and controversy.[4] Both X-ray[5] and neutron[6] powder diffraction studies indicated the compound has a wurtzite structure. There are no features in the infrared[7] or Raman[8] spectra of the solid compound which can be attributed to a copper–hydrogen vibration. Numerous variations[4,9] of the Würtz preparation have involved the reaction of aqueous Cu^{2+} with a variety of reducing agents, but all result in an insoluble copper hydride which contains variable amounts of water that cannot be removed without decomposition of CuH into the elements.

In a recent detailed investigation, soluble copper hydride was found to be monomeric in pyridine solution.[10] In spite of the original claim that soluble and insoluble copper hydride have identical properties, a number of differences were found. X-Ray powder patterns of soluble copper hydride indicated the solid exists in a high degree of subdivision unlike the insoluble form. Also, the pyridine-soluble copper hydride retains variable amounts of pyridine in addition to lesser amounts of copper(I) iodide and traces of LiI. The solubility of copper hydride prepared in this method may be attributed to the presence of pyridine and/or the high degree of subdivision.

With the thought that CuH occurs in pyridine solution as a complex, we have studied the interaction of copper hydride with other potential ligands such as phosphines, phosphites, and 2,2′-bipyridine. With available instrumentation we were unable to locate infrared, Raman, or nmr spectral features characteristic of the hydride in these solutions. Furthermore, we were unable to isolate stable solid copper hydride complexes. Therefore, a cryoscopic investigation was initiated, since this

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appeared to be the only promising method for studying these elusive compounds.

Experimental Section

All manipulations of solvents and compounds were performed under an atmosphere of purified nitrogen by the use of Schlenk, syringe, and drybox techniques.[11] Purification of solvents and the preparation of copper hydride has been described in detail previously.[10] The major contaminant in soluble CuH, residual pyridine, does not affect our results, since the amount of CuH in solution was established by a copper analysis of an aliquot of the solution. Each new preparation of copper hydride was analyzed by pyrolysis (for H_2 and condensables) and EDTA titration (for Cu), and was stored at −196°. The purity was within the limits which we have previously reported for soluble CuH.[10]

Tri-*n*-butylphosphine and tributyl phosphite were distilled under nitrogen prior to use. Trimethyl phosphite, diluted with ethyl ether, was stirred for several hours over sodium wire. Following filtration under nitrogen and removal of the ether under vacuum, the purified phosphite was distilled under nitrogen. 4-Methyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane ("phos") was prepared by the reaction of 2-hydroxymethyl-2-methyl-1,3-propanediol with PCl_3 in tetrahydrofuran.[12] The crude product was sublimed *in vacuo* at 80°: mp 92–94°, lit.[12] 97–98°. 1,2-Bis(diphenylphosphino)ethane (diphos) was prepared by the reaction of lithium diphenylphosphide with 1,2-dichloroethane inte trahydrofuran.[13] *Anal.* Calcd for $C_{26}H_{24}P_2$: H, 6.07; C, 78.38; mol wt, 400. Found: H, 6.02, 6.16; C, 77.76, 77.83; mol wt, 399 (cryoscopically in pyridine). Methyldiphenylphosphine was prepared by the interaction of methylmagnesium iodide with chlorodiphenylphosphine; mol wt, 193 (cryoscopically in pyridine); calcd 200. The integrated ratio of alkyl to aryl protons in the nmr was 3:10. Diethylphenylphosphine was prepared from ethylmagnesium bromide and dichlorophenylphosphine, bp 200°. Butyldiphenylphosphine was obtained in an analogous fashion, and the nmr spectrum of this material displayed the expected ratio of alkyl to aryl protons (9:10). All other ligands were commercial products which were used as obtained.

The cryoscopy apparatus, which is designed for dilute solutions of air-sensitive compounds, has been described previously.[10,11] The procedure used in the cryoscopic titrations follows. Pyridine was weighed into the cryoscopic cell from a syringe and the freezing point of the pure solvent determined. A saturated solution of copper hydride in pyridine was prepared in a 15-ml centrifuge tube fitted with a rubber serum cap. After centrifuging down the excess solid copper hydride, a 10-ml sample was withdrawn by means of a syringe and the needle capped with a silicon rubber plug. One portion of this sample was weighed into the cryoscopic cell, while a second was weighed out for copper analysis (EDTA titration). The freezing point of the copper hydride solution was then determined. A pyridine solution of the ligand to be used in the titration was prepared containing a known weight fraction of ligand. Weighed aliquots of this solution were then added to the cell from a syringe and the freezing point was monitored after each addition.

The freezing point curves exhibited supercooling which was suppressed as described previously.[10,11] Extrapolation of the cooling curves to give the true freezing point was performed by the method of Taylor and Rossini.[14] The initial freezing point depression resulting from the copper hydride solution alone was used to give an apparent molality, m_0. The addition of each increment of ligand gave rise to another molality which was called m_i. For each addition of ligand solution the value of m_0 was corrected for dilution and the ratio of m_i/m_0 was plotted as a function of the molar ratio of ligand to copper hydride.

Since pyridine solutions of copper hydride are known to be unstable at room temperature (CuH in pyridine or tri-*n*-butylphosphine solutions form Cu mirrors after 2 days at room temperature), an experiment was performed to check the stability of a pyridine solution of a copper hydride–phosphine complex. In this experiment, 12 hr at the freezing temperature of pyridine led to a scale change of one unit out of a total depression of 28 units. Also, in many instances the freezing point depression was measured twice after the addition of an increment of phosphine. These results were generally within the expected experimental error, and without any discernible trends. We conclude that the titrations, which were generally completed in less than 8 hr, are not seriously affected by decomposition of the sample.

The hydride content of CuH and solid phosphine complexes was established by pyrolysis of the sample on a vacuum line and collection of the evolved hydrogen with a Toepler pump. While pyrolysis of the sample was generally complete at 100°, heating was continued to a temperature of *ca.* 200°.

Results and Discussion

Monodentate Ligands. The most basic (Table I) readily available phosphine, tri-*n*-butylphosphine, was chosen for initial study. As a test of the technique, copper(I) iodide was titrated with this ligand in pyridine. The molality of copper(I) iodide solutions indicated CuI is monomeric in pyridine. As increments of tri-*n*-butylphosphine were added, the molality of the CuI–phosphine solution remained constant until a phosphine to CuI ratio of 3:1 had been reached (Figure 1). The upward break in the curve after this point indicates the formation of iodotris(triphenylphosphine)copper(I).

Table I. Summary of Cryoscopic Results for Monodentate Ligands and CuH

Ligand	Molality ratio at minimum[a]	ΔHNP[b]
$(H_3CO)_3P$	0.89	520[c]
$H_3CC(-CH_2O-)_3P$	0.82	665[c]
$CH_3(C_6H_5)_2P$	0.82	426[d]
n-$C_4H_9(C_6H_5)_2P$	0.80	397[d]
$(C_2H_5)_2C_6H_5P$	0.52	300[d]
$(n$-$C_4H_9)_3P$	0.45	95[d]

[a] m_i/m_0. [b] The largest half-neutralization potential represents the least basic phosphine. [c] Estimated values from E. M. Thorsteinson, Ph.D. Thesis, Northwestern University, 1966. [d] C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

When copper hydride was treated in a similar manner, the titration curve had a number of unusual features (Figure 2). In the region of ligand to CuH ratio of 0.0–0.5:1, the decreasing molality ratio for the solution indicates an association of the formerly monomeric copper hydride. The degree of association reaches a maximum at a ligand to copper hydride ratio of 0.5:1, and the depth of the minimum in terms of the ratio of apparent molality to the initial molality of the copper hydride solution is 0.5, suggesting the formation of the complex, n-$Bu_3P(CuH)_2$ (eq 1). The rising portion of

$$R_3P + 2CuH = R_3P(CuH)_2 \qquad (1)$$

the curve cannot unambiguously be interpreted from cryoscopic data alone, since it shows either the dissociation of the dimer on addition of more ligand (eq 2), or

$$R_3P + R_3P(CuH)_2 = 2R_3PCuH \qquad (2)$$

the buildup of uncoordinated ligand in solution.

A number of less basic monodentate phosphine and phosphite ligands were investigated to evaluate the effect of changing the nature of the ligand on the dimerization of copper hydride. The resulting curves (Figure 2) have shallower minima than that for tri-*n*-butylphosphine. It will be noted in Table I that there is a general correlation between the molality ratios at the minimum

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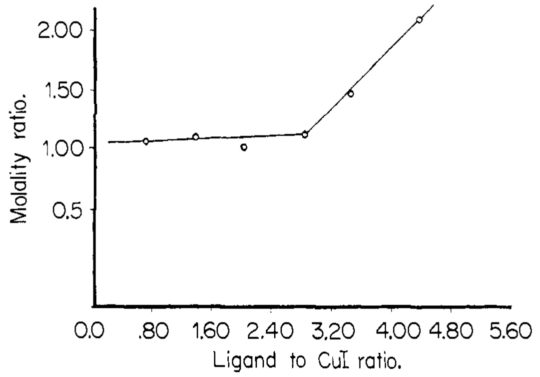

Figure 1. Cryoscopic titration curve of copper(I) iodide with tri-*n*-butylphosphine.

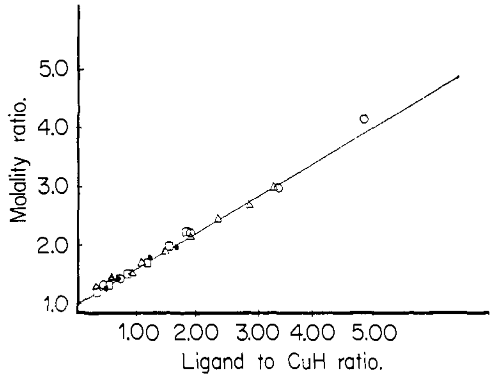

Figure 3. Cryoscopic titration curve of copper hydride with various noninteracting ligands: △, triphenylphosphine; ○, triphenylphosphine sulfide; □, tri-*n*-butyl phosphite; ●, 2,2′-bipyridine.

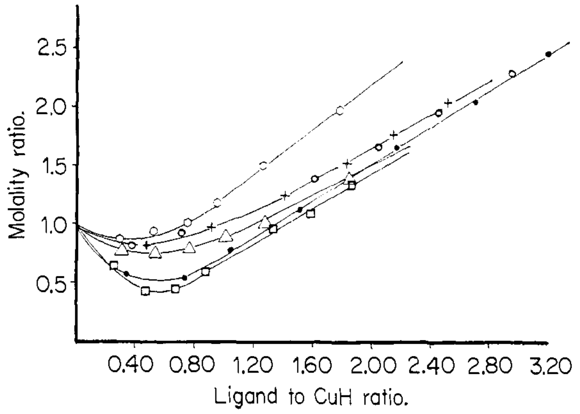

Figure 2. Cryoscopic titration curve of copper hydride with various phosphine and phosphite ligands: □, tri-*n*-butylphosphine; ●, diethylphenylphosphine; ○, butyldiphenylphosphine; +, methyldiphenylphosphine; △, trimethyl phosphite; ○, phos.

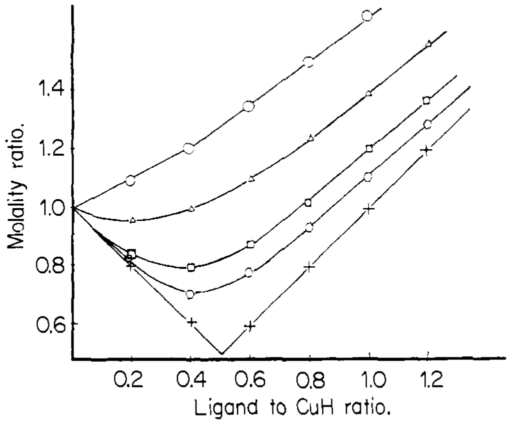

Figure 4. Calculated titration curves for values of the equilibrium constant, $K = [LCu_2H_2]/[L][CuH]^2$: ○, $K = 200$; △, $K = 1200$; □, $K = 8500$; ○, $K = 30{,}000$; +, $K = 10^6$.

and the half-neutralization potentials such that the most basic phosphines have the deepest minima. In addition, triphenylphosphine, triphenylphosphine sulfide, and tri-*n*-butyl phosphite, which all have little basicity, yield titration curves which show no interaction with copper hydride in pyridine solution (Figure 3). However, the correlation with basicity is only approximate and other factors such as softness of the ligand appear to be important.

The simplest interpretation which can be attached to the above results is that the strongest bases also exhibit the largest values of K for the equilibrium in eq 1. The scatter of data points for these dilute solutions of unstable compounds is such that direct calculation of equilibrium constants from the data seemed impractical. Therefore, to provide a basis of comparison with the experimental results, theoretical freezing point depression curves were generated for a series of assumed equilibrium constants, Figure 4. There is qualitative agreement between these curves and the results shown in Figures 2 and 3. In particular, with a decreasing value of K in the theoretical calculations or a phosphine of lower basicity in the experiments, there is a tendency for the minimum to become more shallow and to shift to the left. There is, however, one consistent disparity. The calculated curves indicate that the molality ratio should equal or exceed 1 at a ligand to CuH ratio of 1, but the experimental results, Figure 2, provide a number of examples in which the molality ratio is below 1. This result may be indicative of a small contribution from equilibria involving more than one phosphine per CuH, or it may be a reflection of the small amount of CuI impurity which is generally found in the CuH samples.[10] (It will be recalled that in the experiment with tri-*n*-butylphosphine, 3 moles of phosphine associated with one of CuI.) Thus, the equilibrium given in eq 1 appears to dominate the behavior in pyridine solution, but limited formation of higher adducts may also occur. Interestingly, Costa and coworkers have obtained evidence for dimeric and trimeric phenylcopper complexes with phosphines, *e.g.*, $(C_6H_5)_3P(CuC_6H_5)_{2\text{ or }3}$ and $(n\text{-}C_4H_9)_3P(CuC_6H_5)_2$;[15] these compounds may be analogous to the hydride complexes.

It is probable that dimerization of these Cu(I) species occurs through multicenter bonds. Ignoring coordinated pyridine, which probably is present but cannot be detected by cryoscopy experiments in dilute pyridine solutions, there are only a few reasonable arrangements for the copper, hydrogen, and phosphine moieties in these complexes.

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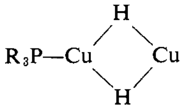
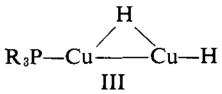


I

$\mathrm{R_3P{-}Cu{-}H{-}Cu{-}H}$

II



III

Structures II and III differ in that the former would arise from an open three-center bond and the latter from a closed three-center bond. There is considerable precedent for three-center hydride bridges from the structures of boron hydrides,[16] transition metal hydrides,[17] and tris(triphenylphosphine)copper(I) borohydride.[18] By contrast, there is no precedent for trialkylphosphine bridges or single Cu(I)–Cu(I) bonds, so structures involving these features are considered less likely than I, II, or III.

The dimerization of CuH when coordinated to the basic phosphines may be related to the phenomenon of induced basicity which is observed with Lewis acids such as BF_3 and GeF_4. When uncoordinated neither of these fluorides has a tendency to self-associate; however, coordination of either molecule to a Lewis base enhances the basicity of the fluorines to the point that they serve as donor sites to additional BF_3 or GeF_4.[19,20] In a similar fashion R_3P–Cu–H may be more basic than Cu–H toward another CuH molecule.

Bidentate Ligands. For comparison with the monodentate ligands the interaction of copper hydride with two bidentate ligands, 2,2′-bipyridine and 1,2-bis(diphenylphosphino)ethane, was investigated. As may be seen in Figure 3, the first of these does not interact with CuH in pyridine solution. By contrast, the diphos ligand yields a distinct V-shaped curve (Figure 5), that has a molality ratio of *ca.* 0.5 at 0.5 diphos per CuH which indicates the formation of diphos$(CuH)_2$. The corresponding monodentate ligand of comparable basicity, diphenylethylphosphine, yields a much shallower titration curve (Figure 2); so we conclude that the diphos ligand probably bridges the two CuH molecules, perhaps with additional hydride bridging to form a cyclic complex.

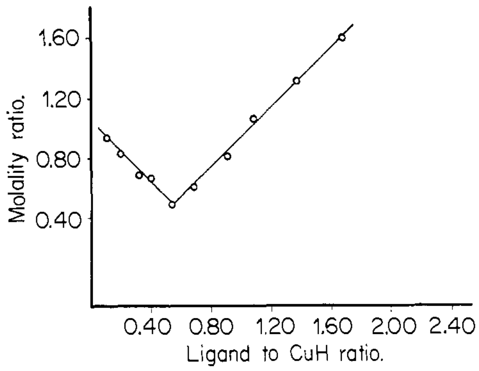


Figure 5. Cryoscopic titration curve of copper hydride with diphos.

Thermal Stability of CuH Complexes. Attempts to isolate solid phosphine complexes of copper hydride were largely unsuccessful due to rapid hydrogen evolution from the solids. For example, the addition of ether to the deep red-brown solution of a triphenylphosphine–copper hydride mixture in benzene results in the formation of a brown to tan precipitate. This precipitate lightens rapidly at room temperature to a cream-colored product, suggesting decomposition. Pyrolysis of one sample resulted in less than one-tenth of the theoretical hydrogen predicted on the basis of the copper analysis (found, 7.1% Cu; calcd for $CuH \cdot 3PPh_3$, 7.5% Cu). Also, solutions of the triphenylphosphine complex in benzene decompose in a matter of hours at room temperature under anerobic conditions. Attempts to prepare copper hydride complexes of tri-*n*-butylphosphine and of 1,2-bis(diphenylphosphino)ethane also led to unstable products. However, the unstable complex of the latter ligand had the approximate composition $(CuH)_2$diphos. *Anal.* Calcd for $C_{26}H_{26}Cu_2P_2$: Cu, 24.1; H (hydridic), 0.38. Found: Cu, 23.0, H (from pyrolysis), 0.42, 0.31.

In a recent note Lutsenko, Kazankova, and Mulkhina claim the preparation of thermally stable phosphine and phosphite complexes of CuH. For some of these, melting points in excess of 100° were reported (*e.g.*, $(P(C_6H_5)_3)_3CuH$, mp 168–170°).[21] Since no preparative details are given, it is not possible to duplicate their work. However, we are inclined to discount this claim of stable hydride complexes because the thermal stabilities are far out of line with our findings, and the elemental analyses which were presented (carbon, total hydrogen, and copper) do not form a convincing case for hydride complexes.

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