vent,[14] such as pyridine, there is a strong increase in magnetic susceptibility with increasing pressure (Table I). This effect is readily explained in terms of the ionization equilibrium

$$Cu_2A_4 + \text{solvent} \overset{P}{\rightleftharpoons} 2Cu^{2+}(\text{solvent}) + 4A^-(\text{solvent}) \qquad (1)$$

where A represents an alkanoate. In pure water copper acetate appears to be almost completely ionized. In agreement with other results,[1,21,22] increasing pressure shifts the equilibrium in favor of the more solvated species. Equilibrium 1 parallels the pressure-dependent equilibria between $CuCl_4^{2-}$ or $CoCl_4^{2-}$ and the solvated Cu^{2+} and Cl^- or Co^{2+} and Cl^- species.[21]

Acknowledgments.—We are indebted to Mr. E. S. Merritt for his assistance with the construction and maintenance of apparatus. E. S. acknowledges financial assistance received under University of Sydney Research Grant R6/66/26.

(21) A. H. Ewald and S. D. Hamann, *Australian J. Chem.*, **9**, 54 (1956).

(22) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworth and Co. Ltd., London, 1957.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
RENSSELAER POLYTECHNIC INSTITUTE, TROY, NEW YORK 12181

Thermodynamics of Copper(I)–Cycloolefin Complex Formation[1]

BY JOSEPH M. HARVILCHUCK,[2a] DAVID A. AIKENS, AND RICHARD C. MURRAY, JR.[2b]

Received October 24, 1968

A convenient and precise method for measurement of complex formation constants of Cu(I) has been developed, based on coulometric generation of Cu(I) and potentiometric measurement of the Cu(I) activity in a $LiClO_4$–2-C_3H_7OH ionic medium. Formation constants and heat of formation values are reported for the 1:1 Cu(I) complexes of a number of cyclic olefins. The logarithmic formation constants of the Cu(I) complexes are linearly related to those of the corresponding Ag(I) complexes. The thermodynamic data for formation of model Cu(I) complexes together with thermodynamic and structural data for the corresponding Ag(I) complexes indicate that the Cu(I) complex of 2,5-norbornadiene is not chelated.

Despite continuous interest in preparation and structural characterization of copper(I)–olefin complexes, little attention has been devoted to the thermodynamics of complex formation. The principal contribution was made by Keefer, Andrews, and Kepner,[3,4] who determined the formation constants of the copper(I) complexes of 20 water-soluble unsaturated alcohols and carboxylic acids. Their value for the formation constant of the allyl alcohol complex has been confirmed by Manahan,[5] who also determined the formation constant of the copper(I)–cyclooctadiene complex.[6] The method used by Keefer, Andrews, and Kepner is based on the increased solubility of cuprous chloride in an aqueous solution of the olefin. This method is limited to water-soluble olefins, and establishment of equilibrium requires 1–2 hr. The method is applicable only to ligands which form copper(I) complexes of sufficient stability to increase the solubility of cuprous chloride substantially, and hence ligands that complex copper(I) weakly cannot be studied. The method used by Manahan is based on the shifts in polarographic half-wave potentials of the Cu(II)–Cu(I) and Cu(I)–Cu(0) waves for stepwise reduction of copper(II) perchlorate in a solution of the ligand in either water or an appropriate nonaqueous solvent. This method avoids the problems of the method of Keefer, Andrews, and Kepner, but the uncertainty of ±0.1 log unit in the formation constants is sufficiently high that estimation of heats of complex formation with reasonable accuracy is virtually impossible.

This paper describes a new approach to measurement of formation constants of copper(I) complexes that avoids the difficulties associated with the earlier methods. A known concentration of copper(I) in a nonaqueous ionic medium is generated by coulometric oxidation of a copper foil, and the copper(I) activity after addition of known concentrations of ligand is measured potentiometrically using a copper amalgam electrode. The method is applied to determination of formation constants and heats of formation of the 1:1 copper(I) complexes of a number of monocyclic and bicyclic monoolefins and diolefins in a 1 *M* lithium perchlorate–2-propanol medium. The results are related to the data for the corresponding silver(I) complexes and to the question of chelation in copper(I) complexes of cyclic diolefins.

Development of the Method

The formation constants of the 1:1 copper(I)–cycloolefin complexes are sufficiently high to ensure essentially complete complexation of copper(I) when free ligand concentrations are in the range 0.01–1 *M*. In

---

(1) Supported in part by a grant from the National Science Foundation. Abstracted in part from the Ph.D. Thesis of J. M. H., Rensselaer Polytechnic Institute, 1966.

(2) (a) NASA Trainee, 1965–1966. (b) NSF Trainee, 1967–1968.

(3) R. M. Keefer, L. J. Andrews, and R. E. Kepner, *J. Am. Chem. Soc.*, **71**, 2381 (1949).

(4) R. M. Keefer, L. J. Andrews, and R. W. Kepner, *ibid.*, **71**, 3906 (1949).

(5) S. E. Manahan, *Inorg. Chem.*, **5**, 482 (1966).

(6) S. E. Manahan, *ibid.*, **5**, 2063 (1966).

this range of ligand concentration, formation of higher complexes can be neglected and limitation of the analytical concentration of copper(I) to 10^{-3} M or less ensures that the free ligand concentration closely approximates the analytical concentration. Then ΔE, the change in potential of a copper amalgam electrode on addition of an analytical concentration of ligand, C_L, to the solution of copper(I), follows directly from the Nernst equation

$$\Delta E = 2.3\frac{RT}{F}(\log K_a C_L)\frac{\gamma_{Cu(I)}}{\gamma_{CuL}}\gamma_L \qquad (1)$$

where K_a is the activity formation constant of the 1:1 copper–olefin complex, CuL, $\gamma_{Cu(I)}$ is the activity coefficient of Cu(I) in 2-propanol, and γ_{CuL} is the activity coefficient of CuL in 2-propanol–olefin solution.

Cycloolefins in 2-propanol deviate substantially from ideal behavior and this fact complicates determination of significant values of activity formation constants. The nonideality is manifested in experimental plots of ΔE *vs.* log C_L, which exhibit slopes significantly below the value required by eq 1. The magnitude of the deviation in slope depends on the identity of the cycloolefin and the temperature and ranges between 2 and 12 mV per decade of cycloolefin concentration. Rigorous assignment of this deviation to individual activity coefficient terms in eq 1 is not possible, but the major cause appears to be a decrease in γ_L with increasing olefin concentration. Alcohol–hydrocarbon solutions exhibit large, positive deviations from Raoult's law,[7] a fact consistent with the observed deviations in the slope of plots of ΔE *vs.* log C_L. Thus for the dilute solutions of cycloolefins of interest, the activity coefficient of the cycloolefin decreases with increasing concentration in accord with the potentiometric results. Assignment of γ_L as the major cause of the nonideal slope is substantiated by the fact that the ideal slope is obtained if a large concentration of a saturated hydrocarbon is present. The factor that controls γ_L thus appears to be the relative change in hydrocarbon concentration. As an example, over the range of 10^{-2} to 1 M cycloolefin, the slope of eq 1 for formation of the 1:1 copper(I)–cyclohexane complex at 25° is increased from 49.8 mV per decade in the absence of inert hydrocarbon to the theoretical value of 59.1 mV per decade in the presence of 3 M cyclohexane. Addition of higher concentrations of cyclohexane decreases the extent of complex formation uniformly but does not change the slope further.

Addition of inert hydrocarbon maintains the activity coefficient of the olefin solute constant in a manner formally analogous to that in which addition of inert electrolyte maintains the activity coefficient of an ionic solute constant. The olefin activity coefficient is maintained constant only at the expense of a substantial increase in the complexity of the medium, however, and this approach has not been used in evaluation of complex formation constants. Instead, concentration formation constants have been calculated by combining the activity coefficient terms in the formation constant. The resulting concentration formation constants, designated K_f, are based on a reference state of 0.01 M cycloolefin in 1 M lithium perchlorate–2-propanol solution, selected for compatibility with the extensive formation constant data reported by Muhs and Weiss[8] for silver(I)–olefin complexes.

Experimental Section

Ionic Medium.—Reagent grade 2-propanol was dried by the method of Lund and Bjerrum,[9] and gas chromatographic analysis indicated that the water content was less than 0.03%. Anhydrous lithium perchlorate was vacuum dried and dissolved in a minimum volume of anhydrous 2-propanol; the solution was held at 0° for 72 hr. The solution was decanted to remove a small quantity of insoluble material and diluted with anhydrous solvent to 1 M concentration. The insoluble material was identified as lithium carbonate, and its removal was necessary to obtain stable potentiometric results.

Cycloolefins.—Olefins except 2-norbornene were refluxed over sodium for 30 min and distilled under nitrogen. The products remained peroxide free for at least 3 hr as judged by the potassium iodide–glacial acetic acid test and were used within this time. 2-Norbornene was purified by bulb to bulb sublimation under vacuum and sealed in evacuated, weighed ampoules. Stock solutions were prepared by breaking the ampoules in a measured volume of deoxygenated electrolyte and were stored under high-purity nitrogen.

Electrodes and Cell.—Copper(I) activity was monitored using a saturated liquid copper amalgam electrode and a silver–silver chloride reference electrode in 1 M $LiClO_4$–0.01 M LiCl in anhydrous 2-propanol prepared as described by Janz and Ives.[10] The anode for coulometric generation of copper(I) was a 99.9% pure copper foil with an area of 25 cm^2 coupled to a platinum foil cathode. The cell was of conventional three-compartment design with provision for nitrogen purging and temperature control to 0.1°. The center compartment contained the copper amalgam indicator electrode and the copper foil generating electrode. The reference electrode and the platinum foil cathode in the end compartments were each isolated from the center compartment by two ultrafine frits.

Procedure.—Copper(I) was generated in the center compartment to a concentration of 10^{-3} M using a calibrated Sargent Model IV coulometric source at a current level of 9.65 mA. Current efficiency, checked periodically by oxidation of the Cu(I) to Cu(II) and titration with EDTA, was 98% or higher. After completion of the generation, the copper foil was removed and known concentrations of the cycloolefin were added through a septum using a calibrated hypodermic syringe. The solution was stirred continuously with a slow stream of nitrogen presaturated with electrolyte. Potentials were measured with a Honeywell Model 2730 potentiometer.

Results

Values of K_f and $\Delta H_f°$, the standard heat of complex formation at 30°, are given in Table I. These values correspond to eq 2 with a reference state of 0.01 M cycloolefin in 1 M lithium perchlorate.

$$\text{L(2-propanol)} + \text{Cu(I)(2-propanol)} \rightleftharpoons \text{Cu(L)(2-propanol)} \qquad (2)$$

Each value of K_f is the mean of three or four deter-

---

[7] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Dover Publications, New York, N. Y., 1964, pp 175–197, 218–219.

[8] M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

[9] H. Lund and J. Bjerrum, *ibid.*, **74**, 3188 (1952).

[10] J. G. Janz and D. J. G. Ives, "Reference Electrodes," Academic Press, New York, N. Y., 1961, Chapter 4.

TABLE I

FORMATION CONSTANTS AND HEATS OF FORMATION FOR COPPER(I)-CYCLOOLEFIN COMPLEXES AT 30°

Olefin	Log K_f	$-\Delta H_f°$, kcal/mol
Cyclopentene	2.86	12.7 ± 0.5
Cyclohexene	2.09	8.3 ± 0.2
Cycloheptene	3.02	7.8 ± 0.5
cis-Cyclooctene	3.46	15.3 ± 0.3
2-Norbornene	4.26	10.8 ± 0.3
1,4-Cyclohexadiene	2.53	7.0 ± 0.4
2,5-Norbornadiene	4.11	15 ± 1

minations with a range of 0.02 log unit or less. Values of $\Delta H_f°$ are based on three or four values of K_f that span a 15° temperature range. The uncertainties in values of K_f and $\Delta H_f°$ are 95% confidence limits as estimated by the least-squares analysis given by Gore[11] for precisely known values of the independent variable. The relatively large uncertainty in values of $\Delta H_f°$ reflects the high sensitivity of the slope to scatter in the points and in principle could be reduced by extending the temperature range. In practice, however, the temperature range is limited to 15° by excessive loss of olefin at higher temperatures and by sluggish establishment of equilibrium at lower temperatures.

Discussion

Comparison with Silver(I) Formation Constants.—The coordination chemistry of copper(I) is known to resemble closely that of silver(I) and these two ions are among the few metals that form stable olefin complexes. This similarity suggests that the formation constants of copper–olefin complexes should be related in a simple manner to the formation constants of the corresponding silver–olefin complexes, but lack of knowledge of the formation constants of olefin complexes of copper(I) has precluded this comparison in the past. The present study makes possible for the first time comparison of formation constants of copper(I)- and silver(I)-olefin complexes over a significant range of values. Two sets of formation constants for silver complexes of cyclic olefins have been reported and are compared with the formation constants of the copper(I) complexes in Figure 1, with log K values of the silver complexes plotted as ordinate and log K_f values of the copper complexes plotted as abscissa. Silver–olefin formation constants reported by Muhs and Weiss,[8] indicated by open circles, are based on measurement of the gas chromatographic retention times of the olefins on a silver nitrate–ethylene glycol column at 40°. Silver–olefin formation constants reported by Traynham and coworkers, indicated by closed circles, are based on measurement of the distribution of the olefins between carbon tetrachloride and aqueous silver nitrate at 25°.

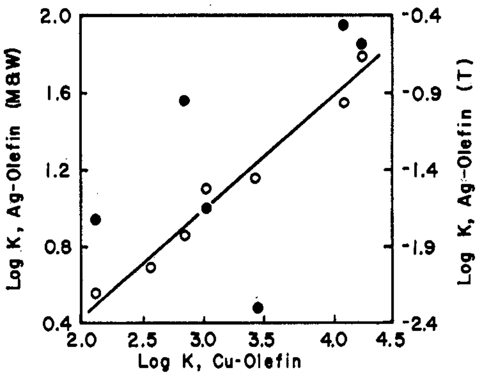


Figure 1.—Correlation of formation constants of Cu(I)–olefin complexes and Ag–olefin complexes: open circles, data of Muhs and Weiss; closed circles, data of Traynham and coworkers.

The principal feature of Figure 1 is the excellent linear correlation between the formation constants for the silver–olefin complexes reported by Muhs and Weiss[8] and the formation constants of the corresponding copper(I)–olefin complexes obtained in this study. The formation constants of the copper(I)–olefin complexes span a range of 2 log units and the formation constant of each copper(I)–olefin complex falls within 0.2 log unit of the line drawn through the points. A somewhat better correlation is obtained if the copper(I)–olefin formation constants are corrected to 40°, but the additional uncertainty introduced by extrapolation of the copper–olefin formation constants to 40° diminishes the advantage of reducing both sets to the same temperature.

In contrast to the strong correlation between the formation constants of the silver–olefin complexes reported by Muhs and Weiss[8] and the formation constants of the corresponding copper(I) complexes, the formation constants of the silver–olefin complexes reported by Traynham[12,13] show virtually no correlation with the formation constants of the corresponding copper(I) complexes. The formation constant reported by Traynham[12] for the silver–cycloheptene complex falls nearly on the correlation line, but formation constants for the other complexes deviate widely and without apparent pattern. The lack of correlation is attributed primarily to the fact that the complex formation reaction as studied by Traynham involves not only formation of the silver–olefin complex but also transfer of the olefin from carbon tetrachloride to water. Thus the formation constants reported are influenced by the free energy of transfer of the olefin, and it would be fortuitous if this contribution depended on the identity of the olefin in the same manner as does the free energy of formation of the silver–olefin complex. By the same token, the strong correlation of the silver–olefin formation constants measured in ethylene glycol medium by Muhs and Weiss[8] with the formation constants of the corresponding copper(I)–olefin complexes measured in 2-propanol medium reflects the similar natures of these two hydroxylic solvents.

The correlation between formation constants of silver and copper(I) olefin complexes shown in Figure 1

---

[11] W. L. Gore, "Statistical Methods for Chemical Experimentation," Interscience Publishers, Inc., New York, N. Y., 1952, pp 131–132.

[12] J. G. Traynham and M. F. Sehnert, *J. Am. Chem. Soc.*, **78**, 4024 (1956).

[13] J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

can be used to estimate silver or copper(I) complex formation constants which are difficult to measure directly. As an example, 1,3-butadiene forms a copper(I) complex, but potentiometric determination of the formation constant is difficult because 1,3-butadiene boils at 4° and tends to be swept out of the cell. The volatility of 1,3-butadiene does not interfere with measurement of the formation constant of the silver complex by the gas chromatographic method, however, and Muhs and Weiss[8] report a log K value of 0.62. This value of the formation constant for the silver complex corresponds to a value of 2.3 log units for the formation constant of the copper(I) complex. This is to be compared to the value of 2.33 log units for the formation constant of the copper(I) complex obtained potentiometrically.

Chelation in Copper(I)–2,5-Norbornadiene.—The question of chelation in the 1:1 silver complex of 2,5-norbornadiene, AgNBD, has been discussed by earlier workers but with divergent conclusions. On the basis of the facile conversion in the solid state of AgNBD to Ag_2NBD and of the stereochemistry of addition products of 2,5-norbornadiene, Traynham and coworkers[13,14] proposed that the AgNBD is not chelated. Muhs and Weiss,[8] on the other hand, proposed on the basis of formation constant data that AgNBD is chelated.

Attempts to establish whether the copper(I)–norbornadiene complex is chelated on the basis of the thermodynamic data in Table I alone do not clearly resolve the question. Evidently, the structure of the olefin does not influence the thermodynamics of complex formation in a simple manner. Hence, comparison of thermodynamic data for complex formation by model compounds, although intuitively appealing, can be misleading and must be looked upon with some skepticism. As an example, consider the formation constants and heat of formation values for the series cyclohexene, 1,4-cyclohexadiene, 2-norbornene, and 2,5-norbornadiene. The formation constant of the 1,4-cyclohexadiene complex is approximately 0.5 log unit larger than that of the cyclohexene complex and the heat of formation of the 1,4-cyclohexadiene complex is approximately 1 kcal less than the heat of formation of the cyclohexene complex. The fact that neither the formation constant nor the heat of formation increases substantially from cyclohexene to cyclohexadiene indicates that the cyclohexadiene complex is not chelated. Comparison of the data for the 1,4-cyclohexadiene and 2,5-norbornadiene complexes reveals that the formation constant and heat of formation of the 2,5-norbornadiene complex exceed the corresponding values for the 1,4-cyclohexadiene complex by approximately 1.5 log units and 8 kcal, respectively. These differences are sufficiently large to suggest strongly that the 2,5-norbornadiene complex is chelated. This conclusion is contradicted, however, by the results of comparing the data for 2-norbornene and 2,5-norbornadiene. Although the heat of formation of the 2,5-norbornadiene complex is approximately 4 kcal greater than the heat of formation of the 2-norbornene complex, the formation constants of the two complexes are essentially equal, a fact that is inconsistent with a chelated structure for the 2,5-norbornadiene complex.

A possible explanation of this apparent inconsistency is that the gross geometry of the olefin, through its effect on the solvation, influences the thermodynamics of complex formation. The positive deviations from Raoult's law characteristic of olefin–alcohol solutions indicate that the olefins tend to be excluded from the hydrogen-bonded structure of the alcohol,[7] and it is reasonable to assume that the degree of exclusion and thus the properties of the olefin are sensitive to the over-all geometry of the individual olefin. In other words, comparisons of thermodynamic data for complex formation are probably more significant for olefins of like geometry such as 2-norbornene and 2,5-norbornadiene and cyclohexene and 1,4-cyclohexadiene than for olefins of much different geometry such as 1,4-cyclohexadiene and 2,5-norbornadiene. Even for olefins of similar geometry, however, the comparison must be a qualitative one, and it is clear that the application of the thermodynamic data to establishment of the structure of the complexes is primarily confirmative rather than predictive.

Definitive evidence for the structure of other metal–cycloolefin complexes applicable to the copper(I)–2,5-norbornadiene complex has been provided by infrared spectroscopy. The X-ray study by Baenziger, Doyle, and Carpenter[15] of the 2,5-norbornadiene–palladium chloride complex has established that the metal is chelated, and the infrared study of the complex by Alexander[16] has demonstrated that the bands at 1550–1650 cm^{-1} characteristic of olefinic bonds are missing. The absence of olefinic bands in the infrared spectrum of $(AgNO_3)_2NBD$, in which both olefinic bonds of 2,5-norbornadiene are coordinated to silver ions, has also been demonstrated by Traynham.[14] Thus the presence of an olefinic band in the 1550–1650-cm^{-1} region of the infrared spectrum of a metal complex of 2,5-norbornadiene indicates that one of the olefinic bonds is not coordinated to the metal ion.

Attempts to isolate the copper(I) complex of 2,5-norbornadiene were unsuccessful. Because the correlation of formation constants of silver(I) and copper(I) complexes in Figure 1 indicates that the structures of the silver(I) and copper(I) cycloolefin complexes are similar, the infrared spectrum of the 1:1 silver complex of 2,5-norbornadiene was obtained. The spectrum was obtained using a mineral oil mull of a mixture containing mostly AgNBD with some Ag_2NBD prepared as described by Traynham.[14] The Ag_2NBD is infrared inactive in the 1550–1650-cm^{-1} region and the presence of a moderately intense olefinic band at 1647 cm^{-1} in the spectrum of the mixture indi-

---

[14] J. G. Traynham, *J. Am. Chem. Soc.*, **83**, 4694 (1961).

[15] N. C. Baenziger, J. R. Doyle, and C. Carpenter, *Acta Cryst.*, **14**, 303 (1961).

[16] R. E. Alexander, *J. Am. Chem. Soc.*, **82**, 535 (1960).

cates that AgNBD is not chelated. It is almost certain, therefore, that the 2,5-norbornadiene complex of copper(I) is also not chelated.

The occurrence or absence of chelation in metal complexes of 2,5-norbornadiene thus appears to depend on the coordination geometry of the metal ion. The chelated structure of the $PdCl_2$ complex of norbornadiene reflects the ability of Pd(II) to form square-planar complexes, with the 2,5-norbornadiene occupying two *cis* coordination sites. The unchelated structures of the copper(I) and silver(I) complexes of 2,5-norbornadiene, on the other hand, reflect the preference of these ions for linear coordination and the inability of 2,5-norbornadiene to occupy two *trans* sites.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF WATERLOO, WATERLOO, ONTARIO, CANADA

Coordination Complexes of Acetylene Diphosphines. I. Diphosphine-Bridged Binuclear Copper(I) and Gold(I) Complexes of Bis(diphenylphosphino)acetylene

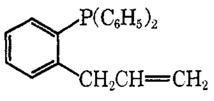
BY A. J. CARTY AND A. EFRATY[1]

Received September 6, 1968

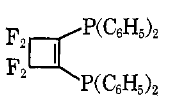
Complexes of the types $(CuX)_2(DPPA)_3$ (X = Cl, Br, I, NO_3, NCS, BH_4; DPPA = bis(diphenylphosphino)acetylene) and $(AuX)_2(DPPA)_n$ (n = 1, X = Cl, Br, I, NCS; n = 3, X = I, NCS; n = 4, X = BF_4, PF_6) have been prepared and characterized. Infrared and Raman spectra of the complexes together with elemental analyses and molecular weight data suggest that the structures are binuclear with bridging bis(diphenylphosphino)acetylene groups. Shifts of the C≡C stretching frequency of the ligand to higher wave number on complexing are consistent with π bonding between the metal and the phosphorus atoms of the ligand.

Introduction

There has been considerable recent interest in the coordinating properties of unsaturated tertiary phosphines and diphosphines.[2-5] Olefinic tertiary phosphines such as *o*-allylphenyldiphenylphosphine (I) are


I

capable of functioning as chelate ligands using the olefinic double bond and the phosphorus atom for coordination.[2] The unusual ligand 1,2-bis(diphenylphosphino)tetrafluorocyclobutene (II) (ffos) behaves


II

as a bidentate chelating agent in complexes with metal halides[3] but reacts with $Fe_2(CO)_9$ to give a compound ffos$[Fe(CO)_3]_2$ in which the double bond coordinates to one $Fe(CO)_3$ group and the two phosphorus atoms coordinate to the other.[6] By contrast, little is known of the ligand properties of acetylenic tertiary phosphines and diphosphines. Moreover, consideration of the linear PCCP skeleton in acetylenic diphosphines of the type $R_2PC{\equiv}CPR_2$ suggests the possibility of markedly different behavior as compared to the chelating ditertiary alkylene or ethylene diphosphines. The present work is part of a program designed to examine synthetic routes to acetylenic phosphines and diphosphines and to investigate their reactions with metal halides, carbonyls, and organometallics. In this paper the synthesis and characterization of a series of novel binuclear copper(I) and gold(I) complexes with the ligand bis(diphenylphosphino)acetylene, $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ (III) (DPPA), are described. A preliminary report of some of this work has already appeared.[7]

Experimental Section

Copper(II) salts were Fisher Reagent grade materials. Chloroauric acid was purchased from British Drug Houses and potassium tetrabromoaurate(III) from K & K Laboratories Inc.

Preparation of Compounds.—Bis(diphenylphosphino)acetylene was prepared by a modification of the method of Hartmann, Beermann, and Czempik.[8] Methylmagnesium chloride (333 ml of a 3 *M* solution in ether) was added to anhydrous ether (370 ml) under a nitrogen atmosphere. A rapid stream of acetylene (previously passed through acetone–Dry Ice traps to remove acetone and moisture) was then passed through the stirred solution at 10° for *ca.* 6 hr. During this period the color changed to light brown. After cooling to 0° diphenylchlorophosphine (205 g, 1 mol) in ether (200 ml) was added slowly to the stirred solution. A saturated solution of ammonium chloride (500 ml) was then added to the dark brown mixture followed by water (1000 ml). The ether layer was separated and evaporated to 250 ml, and ethanol (700 ml) was added. On standing for 24 hr at 0°, colorless crystals of the product appeared. The material was

---

(1) University of Waterloo Postdoctoral Fellow, 1967–1968.

(2) M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *Inorg. Chem.*, **7**, 556 (1968), and references therein.

(3) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *ibid.*, **6**, 2256 (1967).

(4) R. B. King and K. H. Pannell, *ibid.*, **7**, 273 (1968).

(5) H. N. Ramaswamy, H. B. Jonassen, and A. M. Aguiar, *Inorg. Chim. Acta*, **1**, 141 (1967).

(6) W. R. Cullen and C. J. Stewart, unpublished work.

(7) A. J. Carty and A. Efraty, *Can. J. Chem.*, **46**, 1598 (1968).

(8) H. Hartmann, C. Beermann, and H. Czempik, *Z. Anorg. Allgem. Chem.*, **287**, 261 (1956).