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.

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

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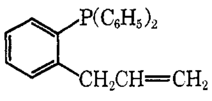
Complexes of the types $(CuX)_2(DPPA)_3$ (X = Cl, Br, I, NO_3, NCS, BH_4; DPPA = bis(diphenylphosphino)acetylene) and $(AuX)_2(DPPA)_n$ (n = 1, X = Cl, Br, I, NCS; n = 3, X = I, NCS; n = 4, X = BF_4, PF_6) have been prepared and characterized. Infrared and Raman spectra of the complexes together with elemental analyses and molecular weight data suggest that the structures are binuclear with bridging bis(diphenylphosphino)acetylene groups. Shifts of the $C\equiv C$ 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.

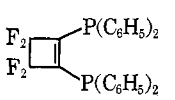
Introduction

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

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[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).

recrystallized from ethanol–chloroform; yield, 192 g (80%); mp 83–84.5° (lit.[8] mp 85.5–86°).

[Tri-μ-bis(diphenylphosphino)acetylene-]dinitratodicopper(I), $(CuNO_3)_2(DPPA)_3$.—A hot solution containing 1.3 g (5.0 mmol) of $Cu(NO_3)_2\cdot 4H_2O$ in absolute ethanol (40 ml) was added dropwise to a solution of III (2.0 g, 5.1 mmol) in ethanol (40 ml). Immediate reduction occurred, and the white crystalline product was filtered off, washed with boiling ethanol and benzene, and dried *in vacuo* at 50°; yield, 1.28 g (36%) (based on weight of metal salt used); mp 214–217 dec. *Anal.* Calcd for $(CuNO_3)_2(DPPA)_3$: C, 65.3; H, 4.2; N, 1.9; mol wt, 1434. Found: C, 65.1; H, 4.2; N, 2.0; mol wt (osmometric in CH_2Br_2), 1297.

[Tri-μ-bis(diphenylphosphino)acetylene-]dichlorodicopper(I), $(CuCl)_2(DPPA)_3$.—The complex was prepared as described above from $CuCl_2\cdot 2H_2O$ and III in ethanolic solution; yield, 40%; mp 335–336° dec. *Anal.* Calcd for $(CuCl)_2(DPPA)_3$: C, 67.8; H, 4.4; Cl, 5.1; mol wt, 1381. Found: C, 67.6; H, 4.4; Cl, 5.3; mol wt (osmometric in CH_2Br_2), 1232.

[Tri-μ-bis(diphenylphosphino)acetylene-]dibromodicopper(I), $(CuBr)_2(DPPA)_3$.—Reaction of $CuBr_2\cdot 2H_2O$ with III in ethanol gave colorless crystals of the complex, yield, 41%; mp 333–336° dec. *Anal.* Calcd for $(CuBr)_2(DPPA)_3$: C, 63.7; H, 4.1; Br, 10.9; mol wt, 1469. Found: C, 63.5; H, 4.3; Br, 11.0 mol wt (osmometric in CH_2Br_2), 1433.

[Tri-μ-bis(diphenylphosphino)acetylene-]diiododicopper(I), $(CuI)_2(DPPA)_3$.—A suspension of $(CuNO_3)_2(DPPA)_3$ (0.2 g, 0.1 mmol) in ethanol (20 ml) was stirred and boiled. To the boiling suspension solid III (0.5 g, 1.3 mmol) was added and the clear solution was allowed to cool to room temperature. This solution on filtering into a saturated ethanolic solution of potassium iodide (20 ml) afforded a white precipitate which was filtered off, washed thoroughly with boiling ethanol to ensure removal of excess ligand, and recrystallized as fine needles from dichloromethane–ethanol; yield, 0.21 g (96%), mp 338–341° dec. *Anal.* Calcd for $(CuI)_2(DPPA)_3$: C, 59.9; H, 3.9; I, 16.2; mol wt, 1564. Found: C, 60.1; H, 3.9; I, 15.8; mol wt (osmometric in CH_2Cl_2), 1648.

[Tri-μ-bis(diphenylphosphino)acetylene-]dithiocyanatodicopper(I), $(CuSCN)_2(DPPA)_3$.—$Cu(NO_3)_2\cdot 4H_2O$ (1.0 g, 5.2 mmol) and a 20-fold excess of potassium thiocyanate were boiled together in ethanol (75 ml) for 5 min and then stirred at room temperature for 12 hr. The suspension was filtered off and the filtrate was added to a warm solution containing III (1.0 g, 2.5 mmol) in ethanol (40 ml). The white precipitate was washed with ethanol and recrystallized from dichloromethane–ethanol; yield, 0.05 g (1.34%); mp 257–260° dec. *Anal.* Calcd for $(CuNCS)_2(DPPA)_3$: C, 67.4; H, 4.2; N, 2.0; mol wt, 1426. Found: C, 67.0; H, 3.9; N, 2.1; mol wt (osmometric in CH_2Br_2), 1287.

[Tri-μ-bis(diphenylphosphino)acetylene-]diborohydridodicopper(I), $(CuBH_4)_2(DPPA)_3$.—Solid ligand III (0.5 g, 1.3 mmol) was added slowly to a boiling suspension of $(CuNO_3)_2(DPPA)_3$ (0.2 g, 0.1 mmol) in ethanol (20 ml). After being cooled to room temperature, the solution was filtered and sodium borohydride (0.15 g, 4.0 mmol) was added. The suspension was warmed to 60° and then allowed to cool to room temperature while stirring for 30 min. The white crystalline material was filtered off, washed with ethanol, and stirred in water for 1 hr to ensure removal of sodium borohydride. Finally the product was recrystallized from dichloromethane–ethanol and vacuum dried at 50°; yield, 0.09 g (47%); mp 154–155° dec. *Anal.* Calcd for $(CuBH_4)_2(DPPA)_3$: C, 69.9; H, 5.1; mol wt, 1337. Found: C, 69.8; H, 5.1; mol wt (osmometric in CH_2Cl_2), 1034.

[μ-Bis(diphenylphosphino)acetylene-]dichlorodigold(I), $(AuCl)_2DPPA$.—Chloroauric acid (1.0 g, 2.6 mmol) was dissolved in ethanol (60 ml) and an ethanolic solution of III (1.0 g, 2.5 mmol) was added. The yellow color of the gold(III) solution rapidly disappeared and a white product was precipitated. Recrystallization from methylene dichloride–ethanol afforded white crystals of the pure material, mp 265–266° dec.

Anal. Calcd for $(AuCl)_2DPPA$: C, 36.4; H, 2.3; Cl, 8.3; Au, 45.9. Found: C, 36.0; H, 2.3; Cl, 9.2; Au, 46.0.

[μ-Bis(diphenylphosphino)acetylene-]dibromodigold(I), $(AuBr)_2DPPA$.—This was prepared in similar fashion to the chloride but with potassium tetrabromoaurate(III) replacing chloroauric acid; mp 284–286° dec. *Anal.* Calcd for $(AuBr)_2DPPA$: C, 33.0; H, 2.1; Br, 16.9; Au, 41.6. Found: C, 32.83; H, 2.0; Br, 17.1; Au, 42.0.

[μ-Bis(diphenylphosphino)acetylene-]diiododigold(I), $(AuI)_2DPPA$.—A solution of $(AuCl)_2DPPA$ (0.25 g, 0.3 mol) in dichloromethane (60 ml) was added to 30 ml of a saturated potassium iodide solution in ethanol. An additional amount of solid potassium iodide (*ca.* 1.0 g) was added and the reaction mixture was stirred at room temperature for 5 hr. The solvent was then removed *in vacuo*, the solid was extracted with dichloromethane, and the solid was filtered off. Addition of ethanol to the filtrate gave white needles of the complex. The material was washed with cyclohexane and dried *in vacuo* at 50°; mp 267–268° dec. *Anal.* Calcd for $(AuI)_2DPPA$: C, 30.0; H, 1.9; I, 24.4; Au, 37.8. Found: C, 30.5; H, 2.1; I, 24.2; Au, 38.1.

[μ-Bis(diphenylphosphino)acetylene-]dithiocyanatodigold(I), $(AuNCS)_2DPPA$.—This complex was prepared from $(AuCl)_2DPPA$ by a metathetical reaction with potassium thiocyanate in a manner similar to that described for the iodide; mp 198–200° dec. *Anal.* Calcd for $(AuNCS)_2DPPA$: C, 37.2; H, 2.2; N, 3.1; Au, 43.6. Found: C, 37.3; H, 2.3; N, 3.0; Au, 43.8.

[Tri-μ-bis(diphenylphosphino)acetylene-]diiododigold(I), $(AuI)_2(DPPA)_3$.—$(AuCl)_2DPPA$ (0.25 g, 0.3 mmol) suspended in boiling ethanol (15 ml) was treated with solid III (0.4 g, 1.0 mmol). The clear solution obtained was cooled to room temperature and a saturated solution of potassium iodide in ethanol was added. Solid potassium iodide (1.0 g) was added and the mixture was stirred for 30 min. After evaporation of the solvent, extraction with dichloromethane and treatment with ethanol yielded the pure product as white needles, mp 217–220°. *Anal.* Calcd for $(AuI)_2(DPPA)_3$: C, 51.2; H, 3.3; Au, 21.5; mol wt, 1830. Found: C, 51.0; H, 3.6; Au, 21.1; mol wt (osmometric in CH_2Cl_2), 1825.

[Tri-μ-bis(diphenylphosphino)acetylene-]dithiocyanatodigold(I), $(AuNCS)_2(DPPA)_3$.—The complex was prepared as described for the iodide with potassium thiocyanate replacing potassium iodide; mp 194–195° dec. *Anal.* Calcd for $(AuNCS)_2(DPPA)_3$: C, 56.8; H, 3.6; N, 1.7; Au, 23.3; mol wt, 1692. Found: C, 56.4; H, 3.7; N, 1.7; Au, 23.4; mol wt (osmometric in CH_2Cl_2), 1693.

Attempts to isolate the corresponding bromide by treatment of $(AuCl)_2DPPA$ with excess ligand followed by potassium bromide were unsuccessful. No precipitate formed and removal of solvent from the reaction mixture yielded only starting materials. Similarly, no chloride complex of the formula $(AuCl)_2(DPPA)_3$ could be isolated from the solution of $(AuCl)_2DPPA$ and excess ligand in ethanol.

[Tetra-μ-bis(diphenylphosphino)acetylene-]ditetrafluoroboratodigold(I), $(AuBF_4)_2(DPPA)_4$.—$(AuCl)_2DPPA$ (0.25 g, 0.3 mmol) and III (0.4 g, 1.0 mmol) were boiled together in ethanol (20 ml). The clear solution was cooled and filtered, and a saturated solution of sodium tetrafluoroborate (20 ml) was added to give a white precipitate. A further quantity of the tetrafluoroborate (1.0 g) was added and the mixture was stirred at room temperature for 30 min. The solid product was extracted with dichloromethane and ethanol was added to the solution. Slow evaporation of the solvent afforded the pure complex; mp 245–248° dec. *Anal.* Calcd for $(AuBF_4)_2(DPPA)_4$: C, 58.3; H, 3.8; P, 11.6; Au, 18.3; mol wt, 2143. Found: C, 58.1; H, 3.9; P, 11.4; Au, 18.7; mol wt (osmometric), 1969 (in CH_2Cl_2), 816 (in CH_3NO_2).

[Tetra-μ-bis(diphenylphosphino)acetylene-]dihexafluorophosphatodigold(I), $(AuPF_6)_2(DPPA)_4$.—The preparation was similar to the above with potassium hexafluorophosphate in place of sodium tetrafluoroborate. The product was recrystallized twice from dichloromethane–ethanol; mp 238–241° dec. *Anal.* Calcd for $(AuPF_6)_2(DPPA)_4$: C, 55.3; H, 3.6; Au, 17.4; mol wt, 2260. Found: C, 54.7; H, 3.5; Au, 17.3; mol wt (osmometric), 1845 (in CH_2Cl_2), 935 (in CH_3NO_2).

Physical Measurements.—Infrared spectra in the range 4000–600 cm^{-1} were recorded on a Beckman IR-9 spectrophotometer as Nujol or hexachlorobutadiene mulls between sodium chloride windows. Spectra were calibrated with polystyrene, and frequencies are accurate to ± 2 cm^{-1}. In the region 400–200 cm^{-1} a Beckman IR-12 spectrophotometer was used. Samples were examined as Nujol mulls between polyethylene plates.

Raman spectra of the solid complexes were measured on a helium–neon gas laser Raman spectrophotometer using the 6328-Å exciting line. In some cases spectra were unobtainable owing to the strong fluorescence of the sample. Calibrations were made using the 6518-Å line of carbon tetrachloride and frequencies are accurate to ± 2 cm^{-1}.

Conductivity measurements were made at 23° in nitromethane using a Beckman conductivity bridge and a cell with polished platinum electrodes of cell constant 0.2779. Microanalyses were carried out by A. B. Gygli, Toronto, Canada, and by Alfred Bernhardt, Mülheim, Germany. Gold was estimated gravimetrically by direct ignition. Molecular weights were measured osmometrically in dichloromethane, nitromethane, and dibromomethane.

Results and Discussion

Copper Complexes.—Ligand III rapidly reduces solutions of copper(II) salts with the formation of colorless diamagnetic complexes of the general formula $(CuX)_2(DPPA)_3$ (X = Cl, Br, I, NO_3, NCS, BH_4). (Good quality nmr spectra were obtained for the complexes in deuteriochloroform.) The compounds are virtually insoluble in the polar solvents ethanol, nitromethane, and acetonitrile but dissolve readily in dichloromethane from which they can be recrystallized. Some dissociation apparently occurs in dibromomethane, however, since molecular weights in this solvent are slightly lower than the values expected for the binuclear $(CuX)_2(DPPA)_3$ species.

Infrared Spectra.—The infrared spectra of the ligand and the complexes between 2500 and 650 cm^{-1} are shown in Table I. The spectra of $(CuX)_2(DPPA)_3$ (X = Cl, Br, I) are very similar to the spectrum of the uncomplexed ligand, the only noteworthy changes being an increase in intensity and shift to higher frequency of the 1090-cm^{-1} ligand absorption on coordination and the appearance of an extra, weak band in the region 1570–1600 cm^{-1} in the complexes. The 1090-cm^{-1} absorption is characteristic of the group $P-C_6H_5$ and similar changes in intensity and frequency have been shown to occur on coordination of triphenylphosphine and related phosphines.[9,10]

$\nu(C\equiv C)$ is infrared inactive in III since it is a symmetrical disubstituted acetylene. However, coordination of a symmetrical acetylene to a transition metal results in a lowering of symmetry around the triple bond and causes $\nu(C\equiv C)$ to appear weakly in the infrared spectrum at a frequency 200–400 cm^{-1} lower than in the free ligand.[11,12] The absence of any bands between 2300 and 1600 cm^{-1} attributable to $\nu(C\equiv C)$ of a coordinated triple bond strongly suggests that only the phosphorus atoms of the ligand are attached to the metal. Moreover, if the diphosphine was acting as a monodentate ligand in these complexes an absorption due to $C\equiv C$ stretching would appear in the infrared spectrum at *ca.* 2100 cm^{-1}.[13] The results are therefore consistent with III behaving as a bidentate ligand in which the acetylenic triple bond is uncoordinated.

Table I

Infrared Spectra (2500–650 cm^{-1}) of DPPA and Copper(I) Complexes

DPPA

1580 w, 1478 m, 1433 s, 1304 w, 1275 vw, 1179 vw, 1154 w, 1090 m, 1067 w, 1023 w, 998 w, 967 vw, 913 vw, 827 s, 752 vs, 742 vs, 695 vs

$(CuNO_3)_2(DPPA)_3$

1590 w, 1580 w, 1483 m, 1440 vs, br, 1296 vs, br, 1187 m, 1172 m, 1098 m, 1028 m, 1000 w, 970 vw, 839 m, 818 sh, 755 sh, 740 s, 723 sh, 692 s

$(CuCl)_2(DPPA)_3$

1585 w, 1570 w, 1481 m, 1437 s, 1309 vw, 1183 w, 1159 w, 1126 vw, 1097 m, 1070 w, 1031 w, 1000 w, 973 w, 920 vw, 841 s, 752 sh, 741 vs, 726 sh, 695 vs

$(CuBr)_2(DPPA)_3$

1583 w, 1577 w, 1481 m, 1437 s, 1182 w, 1159 w, 1098 m, 1070 w, 1031 w, 1000 w, 973 w, 842 s, 752 sh, 741 vs, 726 sh, 6977 vs

$(CuI)_2(DPPA)_3$

1584 w, 1570 w, 1480 m, 1437 m, 1306 vw, 1180 w, 1157 w, 1094 m, 1028 w, 1000 w, 972 w, 834 s, 751 m, 738 s, 690 vs

$(CuNCS)_2(DPPA)_3$

2060 s, 1578 w, 1482 m, 1438 s, 1306 vw, 1182 w, 1156 w, 1090 m, 1062 w, 1022 w, 996 w, 830 s, 805 w, 798 w, 745 sh, 730 s, 684 vs

$(CuBH_4)_2(DPPA)_3$

2368 m, 2340 s, br, 1996 m, br, 1588 w, 1577 w, 1482 m, 1438 s, 1310 w, 1189 w, 1161 w, 1130 w, 1097 m, 1067 m, br, 1030 w, 1002 w, 975 w, 840 s, 755 m, 745 s, 696 vs

For the complex $(CuNO_3)_2(DPPA)_3$ additional bands due to the nitrate group appear in the spectrum. In the spectra of ionic nitrates, $\nu_3(E')$ occurs as a strong broad band at *ca.* 1390 cm^{-1}.[14] There is no band in this region in the complex but the presence of two strong bands at 1440 and 1296 cm^{-1} confirms that the nitrate is coordinated to the copper. On the basis of a monodentate nitrate group, these bands are assignable to $\nu_4(B_1)$ and $\nu_1(A_1)$, respectively. Similarly, a medium-intensity band at 1028 cm^{-1} which overlaps a weak ligand absorption may arise from $\nu_2(A_1)$ and a weak band at 818 cm^{-1} may be assigned to $\nu_6(B_2)$ of the nitrato group. It must be emphasized, however, that without Raman polarization data[15] it is not possible to determine positively whether the nitrate is mono- or bidentate in this compound. The similarity in spectra and properties of all of the compounds $(CuX)_2$-

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[9] A. J. Carty, *Can. J. Chem.*, **45**, 345 (1967).

[10] G. B. Deacon and J. H. S. Green, *Chem. Ind.* (London), 1031 (1965).

[11] J. Chatt, R. G. Guy, and L. A. Duncanson, *J. Chem. Soc.*, 827 (1961).

[12] F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968).

[13] For example, in $(C_6H_5)_2P^+(CH_3)C\equiv CP(C_6H_5)_2,I^-$ $\nu(C\equiv C)$ appears as an intense band at 2108 cm^{-1} in the infrared spectrum.

[14] C. C. Addison and N. Logan, *Advan. Inorg. Chem. Radiochem.*, **6**, 71 (1964).

[15] C. C. Addison and D. Sutton, *Progr. Inorg. Chem.*, **8**, 195 (1967).

$(DPPA)_3$ does, however, suggest that they have similar structures. Hence, a monodentate nitrato group seems most probable.

$(CuNCS)_2(DPPA)_3$ has a single, sharp $\nu(C\equiv N)$ absorption at 2060 cm^{-1} and two weak $\nu(C—S)$ bands at 798 and 805 cm^{-1}. Recent work[16] has shown that in amine complexes of copper(I) thiocyanate containing S-bonded thiocyanate, $\nu(C\equiv N)$ absorptions occur in the range 2085–2150 cm^{-1} and $\nu(C—S)$ appears between 732 and 750 cm^{-1}. N-bonded isothiocyanate in copper(II)–amine complexes shows $\nu(C\equiv N)$ absorption in the narrow range 2060–2109 cm^{-1} and $\nu(C–S)$ between 792 and 827 cm^{-1}.[16,17]

Thus it is reasonable to conclude that in $(CuNCS)_2(DPPA)_3$, the thiocyanate is N bonded. This is an interesting result since in amine complexes thiocyanate is S bonded to copper(I). Similar results have been obtained for platinum(II) complexes of the type $Pt(SCN)_2L_2$ (L = amine, phosphine) where thiocyanate is also N bonded when L = phosphine but S bonded when L = amine.[18] In terms of the hard and soft theory of acids and bases,[19] the soft acids Cu(I) and Pt(II) prefer the hard anion NCS^- when coordinated by the soft bases phosphines but the soft anion SCN^- when coordinated by the hard bases amines.

The infrared spectrum of $(CuBH_4)_2(DPPA)_3$ in addition to DPPA absorptions shows bands in the range 2370–1990 cm^{-1} owing to coordinated borohydride. Lippard[20] has recently prepared a series of copper(I) borohydride complexes of the type $L_2Cu(BH_4)$ (L = triarylphosphine). An X-ray investigation showed that in the triphenylphosphine complex, a distorted tetrahedral configuration around the copper was attained with two hydrogen atoms of the borohydride coordinated to each copper atom.[21] Terminal B–H stretching modes were assigned to bands at 2392–2343 cm^{-1} while bridging B–H modes occurred between 2018 and 1924 cm^{-1}.[20] In a similar fashion we assign bands at 2368 and 2340 cm^{-1} to $\nu_{terminal}(B–H)$ and the broad absorption centered on 1996 cm^{-1} must arise from $\nu_{bridging}(B–H)$. In theory it ought to be possible to differentiate a monodentate BH_4 group (C_{3v}) from a bidentate BH_4 group (C_{2v}) since in the former case only a single B–H bridging mode (A_1) is expected compared with two modes ($A_1 + B_1$) for the bidentate species. The presence of only one band for $(CuBH_4)_2(DPPA)_3$ may indicate a monodentate borohydride but the absorption is broad and may contain two unresolved peaks.

Far-Infrared Spectra.—Metal–halogen stretching frequencies are often useful as an aid to determining the stereochemistry of coordination compounds.[22] We have measured the far-infrared spectra of DPPA and the halide complexes in the region 400–200 cm^{-1} (Table II) in an attempt to obtain stereochemical information. Comparison of the analogous complexes shows that $\nu(Cu–Cl)$ appears as a single, strong band at 267 cm^{-1} and $\nu(Cu–Br)$ at 202 cm^{-1}. These values are as expected lower than the frequency ranges for $\nu(Cu–X)$ in tetrahedral copper(II) complexes[23] and agree with a tetrahedral C_{3v} configuration of three phosphorus atoms and one halide around each copper atom where a single $\nu(Cu–X)$ (A_1) mode is expected.

TABLE II

FAR-INFRARED SPECTRA (400–200 CM^{-1}) OF DPPA COMPLEXES OF COPPER(I) AND GOLD(I)

Compound	Frequency, cm^{-1}
DPPA	370 m, 341 w, 305 vw, 386 vw, 262 vw, 247 w
$(CuCl)_2(DPPA)_3$	382 w, 331 vw, 302 w, 267 vs[a]
$(CuBr)_2(DPPA)_3$	383 m, 332 w, 205 w, 260 w, 250 w, 202 vs[a]
$(CuI)_2(DPPA)_3$	384 w, 380 vw, 312 w, 255 w
$(AuCl)_2(DPPA)$	382 vw, 355 w, 328 s,[a] 305 w, 280 w
$(AuBr)_2(DPPA)$	384 w, 361 w, 305 w, 253 w, 240 s[a]
$(AuI)_2(DPPA)$	384 w, 360 w, 308 w, 280 w, 229 vw
$(C_6H_5)_3PAuCl$	329,[a] 323[a,b]
$(C_6H_5)_3PAuBr$	233[a,b]

[a] Absorption due to $\nu(M–X)$. [b] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

Raman Spectra.—These compounds are ideally suited for Raman measurements as they are colorless and readily soluble in methylene dichloride. Raman shifts measured in solution were almost identical with those obtained from the solids using the 6328-Å exciting line of the He-Ne laser. Values in Table III refer to the solids. $\nu(C\equiv C)$ was readily identified in all of the spectra as a very strong symmetrical absorption just above 2100 cm^{-1}. The results provide conclusive evidence that the triple bond remains uncoordinated on complex formation, $\nu(C\equiv C)$ occurring 20–30 cm^{-1} higher in the complexes than in the free ligand.

TABLE III

RAMAN SHIFTS (CM^{-1}) OF $\nu(C\equiv C)$ IN DPPA COMPLEXES OF COPPER(I) AND GOLD(I)

Compound	$\nu(C\equiv C)$, cm^{-1}	Compound	$\nu(C\equiv C)$, cm^{-1}
DPPA	2097	$(AuCl)_2(DPPA)$	2136
$(CuCl)_2(DPPA)_3$	2124	$(AuBr)_2(DPPA)$	2131
$(CuBr)_2(DPPA)_3$	2120	$(AuI)_2(DPPA)$	. . .[a]
$(CuI)_2(DPPA)_3$	2123	$(AuNCS)_2(DPPA)$	. . .[a]
$(CuNO_3)_2(DPPA)_3$	2125	$(AuI)_2(DPPA)_3$	2117
$(CuNCS)_2(DPPA)_3$	2121	$(AuNCS)_2(DPPA)_3$	2120
$(CuBH_4)_2(DPPA)_3$	2120	$(AuBF_4)_2(DPPA)_4$	2113
		$(AuPF_6)_2(DPPA)_4$	2117

[a] Spectrum unobtainable owing to fluorescence of sample.

The molecular geometry of diphosphines of the type $R_2PC\equiv CPR_2$ is such that chelating properties are unlikely. Thus, using the recent X-ray data on $P(C\equiv CC_6H_5)_3$,[24] the distance between the two phosphorus atoms in the linear PCCP skeleton of III can be calculated as 4.7 Å. The corresponding distance

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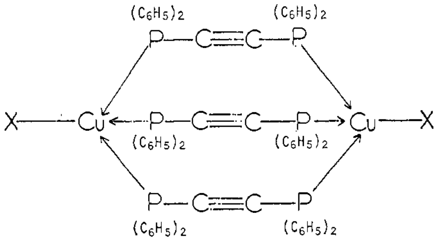
in the chelating diphosphine *o*-phenylenebis(diethylphosphine) is 3.1 Å. To our knowledge only two X-ray structural determinations have been carried out on tetrahedral copper(I) phosphine complexes[21,25] and in both cases the P–Cu–P bond angle is unusually large. For $[(C_6H_5)_3P]_2CuNO_3$ the P–Cu–P angle is 131.1° and the P–P distance along the tetrahedral edge is 4.10 Å.[25] Much smaller distances are found for example between phosphorus atoms in *cis* square-planar platinum(II) complexes.[26] The 4.7-Å bite of the ligand is clearly too large for acetylenic diphosphines of this type to chelate in the same way as alkylene diphosphines. The linear geometry is, however, excellent for bridging between two metal atoms.

We have now prepared complexes of DPPA with Cu(I) Ag(I), Au(I), Au(III), Pd(II), Pt(II), Pt(IV), Rh(III), Ir(III), and Ir(I) halides and with a variety of cyclopentadienylmetal carbonyls. Binuclear complexes having bridging bis(diphenylphosphino)acetylene groups have been obtained in all cases. For the copper(I) complexes described herein, the ligand geometry, analytical data, molecular weight measurements, and infrared and Raman spectra all point to a symmetrical structure (IV) in which three diphosphine ligands bridge two tetrahedral copper atoms, the local symmetry around each metal atom being C_{3v}.



IV

The related tetrahedral complexes $CuX((C_6H_5)_3P)_3$ and $Cu_2X_2((C_6H_5)_3P)_3$ (X = Cl, Br, I) are known[27] and several other tetrahedral phosphine complexes of copper(I) have been described in recent years.[28] By contrast, few diphosphine complexes have been prepared and for the known compounds Cu(diphos)X [diphos = 1,2-bis(diphenylphosphino)ethane; X = Cl, I, BH_4] structural data are lacking.[28] It is interesting to note that reaction of copper(II) halides with tertiary phosphines or diphosphines gives only copper(I) phosphine complexes, and no copper(II) compounds have yet been characterized. The earlier reported copper(II) compounds $(CH_3(C_6H_5)_2As)_3Cu_2Cl_3$[29] and $(Cy_3P)_2CuCl_2$[30] (Cy_3P = tricyclohexylphosphine) have since been shown[31,32] to be arsine oxide and phosphine oxide complexes. The stability of the copper(I) complexes over their copper(II) counterparts must be in some measure related to the strength of the copper(I)–phosphorus bond. Since copper(I) is unlikely to form stronger σ bonds with phosphorus than copper(II), the driving force for the reduction copper(II) → copper(I) may well be the increased π contribution to the Cu–P bond from dπ–dπ (Cu–P) back-bonding in the copper(I) species.

Gold Complexes.—Monodentate tertiary phosphines form stable complexes of the type $AuX(PR_3)$ (X = Cl, Br, I, CH_3, C≡CR, $(C_6H_5)_3Ge$; R = alkyl, aryl).[33–36] Recent work has shown that triphenylphosphine also gives three- and four-coordinate gold(I) compounds under appropriate conditions.[37] The diphosphines $R_2PCH_2CH_2PR_2$ (R = C_2H_5, C_6H_5) (diphos), however, react with chloroauric acid to give the binuclear diphosphine-bridged complexes ClAu(diphos)AuCl[38,39] in contrast to the ligand *o*-diethylphosphino(diethylarsino)benzene (PAs) which produces the ionic tetrahedral compounds $[Au(PAs)_2]X$ with gold(I) halides.[40]

Chloroauric acid reacts with bis(diphenylphosphino)acetylene (DPPA) in ethanolic solution to give a colorless diamagnetic complex of empirical formula $(AuCl)_2$DPPA. The analogous complexes $(AuX)_2$(DPPA) (X = I, NCS) can be prepared by metathesis of the chloride complex with potassium iodide or thiocyanate. Attempts to prepare a bromide by this technique failed, but the compound can be readily obtained by reduction of potassium tetrabromoaurate with ligand in ethanol. The freshly prepared complexes are soluble in dichloromethane, but this solubility drops off markedly on drying. Molecular weight measurements were impractical owing to insolubility in suitable solvents except for the iodide where measurements at low concentration in dichloromethane indicate the presence of $(AuI)_2$DPPA in solution. The infrared spectra of the complexes $(AuX)_2$DPPA (X = Cl, Br, I) in the range 1600–600 cm^{-1} are similar to the spectrum of the free ligand (Table IV), the most notable changes being a resolution of the strong bands at 752, 742, and 695 cm^{-1} into several medium-intensity bands in $(AuCl)_2$DPPA and an increase in intensity of the 1090-cm^{-1} band in all of the complexes. Similar changes were noted with the copper(I) complexes.

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Table IV

Infrared Spectra (2200–650 cm^{-1}) of DPPA and Gold(I) Complexes

DPPA

1580 w, 1478 m, 1433 s, 1304 w, 1275 vw, 1179 vw, 1154 w, 1090 m, 1067 w, 1023, w, 998 w, 967 vw, 913 vw, 827 s, 752 vs, 742 vs, 695 vs

(AuCl)$_2$(DPPA)

1582 vw, 1472 vw, 1480 m, 1437 s, 1312 w, 1191 w, 1159 w, 1102 m, 1024 vw, 1000 w, 837 s, 761 m, 751 m, 740 m, 725 w, 702 m, 694 m, 682 m

(AuBr)$_2$(DPPA)

1582 vw, 1572 vw, 1478 m, 1437 s, 1310 w, 1175 w, 1100 m, 1021 w, 998 w, 971 w, 923 w, 831 s, 743 s, 711 m, 690 s

(AuI)$_2$(DPPA)

1582 vw, 1570 vw, 1479 m, 1435 s, 1303 w, 1177 w, 1159 w, 1100 s, 1024 w, 998 w, 962 w, 920 vw, 834 s, 742 s, 725 w, 711 m, 690 s

(AuNCS)$_2$(DPPA)

2112 s, 1590 w, 1585 vw, 1478 m, 1310 w, 1214 w, 1160 w, 1100 m, 1024 w, 1000 w, 915 w, 834 s, 814 m, 742 s, 730 m, 705 m, 684 s

(AuI)$_2$(DPPA)$_3$

1582 w, 1570 w, 1480 m, 1434 s, 1328 vw, 1310 vw, 1184 w, 1159 w, 1099 m, 1070 w, 1028 w, 1000 w, 981 vw, 840 s, 752 s, 740 s, 692 s

(AuNCS)$_2$(DPPA)$_3$

2095 s, 1584 w, 1570 w, 1479 m, 1306 w, 1163 w, 1096 m, 1025 w, 998 w, 970 w, 840 s, 762 s, 740 s, 725 w, 691 s

(AuBF$_4$)$_2$(DPPA)$_4$

1582 w, 1578 w, 1480 m, 1436 s, 1305 w, 1280 w, 1218 w, 1182 w, 1160 w, 1092 m, 1058 s, 1025 sh, 1024 sh, 998 m, 842 s, 828 s, 754 s, 740 s, 692 s

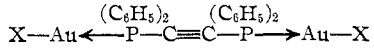
(AuPF$_6$)$_2$(DPPA)$_4$

1584 w, 1570 w, 1480 m, 1310 w, 1184 vw, 1160 w, 1098 m, 1020 w, 1028 w, 1000 m, 865 m, 842 vs, 755 s, 742 s, 690 s

For (AuNCS)$_2$DPPA, a strong, sharp absorption at 2112 cm^{-1} due to ν(C≡N) confirms the presence of coordinated thiocyanate. Although this may suggest Au—S bonding rather than Au—N since ν(C≡N) in S-bonded thiocyanates is generally at >2100 cm^{-1},[18] we were unable to confirm it by analysis of the C—S stretching region or the NCS bending region owing to the occurrence of strong ligand absorptions between 650–850 and 400–500 cm^{-1}. The presence of S-bonded thiocyanate is not predictable, however, because in metal–thiocyanate–phosphine complexes, M—NCS bonding predominates.[41] Moreover, thiocyanate is N bonded in (CuNCS)$_2$(DPPA)$_3$. We are at present preparing a variety of phosphine and amine complexes of gold(I) in an attempt to deduce the nature of the metal–thiocyanate bond from infrared correlations.

The absence of ν(C≡C) in the infrared spectra of the complexes (AuX)$_2$DPPA and the appearance of this vibration in the Raman spectrum at a frequency 30–40 cm^{-1} higher than in the free ligand (Table III) suggests that the ligand is coordinated *via* both phosphorus atoms but that the acetylenic triple bond is uncoordinated. The far-infrared spectra of the complexes (AuX)$_2$(DPPA) (X = Cl, Br, I) (Table II) are strongly indicative of the presence of dicoordinate gold. Comparison of ligand and complex spectra shows that ν(Au—Cl) appears at 328 cm^{-1} and ν(Au—Br) at 240 cm^{-1} with ν(Au—I) below 200 cm^{-1}. These values are close to those found by Coates and Parkin[42] for other linear gold–phosphine complexes of the type (R$_3$P)AuX.

We have previously pointed out that the linear PCCP skeleton and the "bite" of 4.7 Å suggest that III is incapable of chelation. The compounds (AuX)$_2$DPPA are therefore formulated as binuclear species (V) in which the diphosphine behaves as a bridging group. Similar structures were proposed for the



$$\mathrm{X{-}Au \longleftarrow \overset{(C_6H_5)_2}{P}{-}C{\equiv}C{-}\overset{(C_6H_5)_2}{P} \longrightarrow Au{-}X}$$

V

compounds (AuCl)$_2$(diphos) [diphos = 1,2-bis(diphenylphosphino)ethane or 1,2-bis(diethylphosphino)ethane] although no definite structural evidence was presented.[38,39] It is interesting to note that gold(I) appears to have a stronger tendency to form linear complexes than copper(I) since salts of the latter react with 1,2-bis(diphenylphosphino)ethane to yield complexes of the type CuX(diphos)[24] and with III to give (CuX)$_2$(DPPA)$_3$, but not (CuX)$_2$DPPA.

The complex (AuCl)$_2$(DPPA) is readily soluble in hot ethanol in the presence of a large excess of ligand. From this solution (AuI)$_2$(DPPA)$_3$ and (AuNCS)$_2$(DPPA)$_3$ can be readily precipitated on addition of the appropriate potassium salt although no evidence could be obtained for the solid compounds (AuCl)$_2$(DPPA)$_3$ and (AuBr)$_2$(DPPA)$_3$. Mann and his coworkers[40] have also noticed that gold(I)–chloride–phosphine complexes of coordination number greater than 2 are more difficult to prepare than the corresponding iodides and have attributed the effect to the class b character of gold(I).

Molecular weight measurements indicate the presence of the binuclear species (AuX)$_2$(DPPA)$_3$ in solution. ν(C≡N) appears at 2095 cm^{-1} in the infrared spectrum of (AuNCS)$_2$(DPPA)$_3$ which may indicate Au—NCS bonding, but as in the case of (AuNCS)$_2$(DPPA), no confirmation of this could be obtained. The infrared spectra (2100–650 cm^{-1}) (Table IV) and the presence of ν(C≡C) in the Raman spectrum near 2120 cm^{-1} confirm that both phosphorus atoms of the ligand are coordinated but that the triple bond is not. The most probable structure for the complexes (AuX)$_2$(DPPA)$_3$ is therefore VI in which three diphosphine molecules symmetrically bridge two tetrahedral gold(I) atoms. The compounds thus resemble (CuX)$_2$(DPPA)$_3$ (X = Cl, Br, I, NCS). Other tetrahedral gold(I) phosphine complexes have been prepared but only with noncoordinating anions such as perchlorate or tetraphenylborate[37] or when chelating ligands are present.[40]

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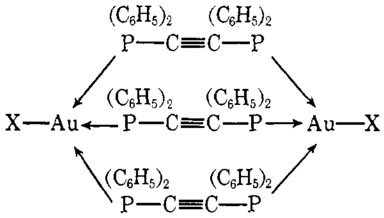
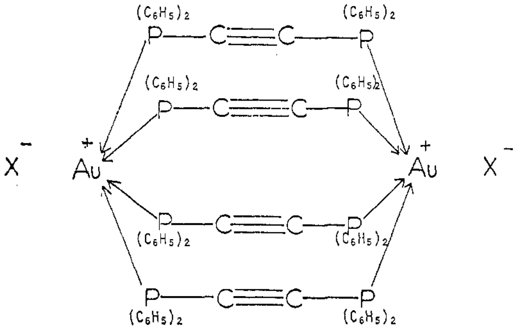
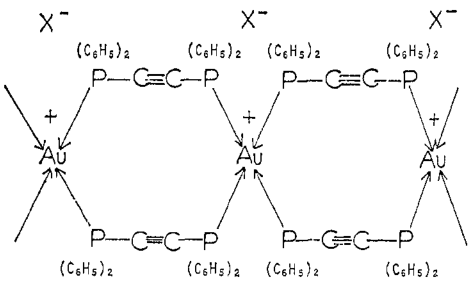


VI

The compounds of empirical formula $(AuX)(DPPA)_2$ ($X = BF_4$, PF_6) are readily precipitated from ethanolic solutions of $(AuCl)_2DPPA$ and excess ligand by addition of sodium tetrafluoroborate or potassium hexafluorophosphate. Infrared spectra confirm that the complexes contain ionic tetrafluoroborate and hexafluorophosphate, $\nu_3(T_2)$ of BF_4^- occurring as a strong band at 1058 cm^{-1} and $\nu_3(T_{1u})$ of PF_6^- at 842 cm^{-1}. No resolution of these two bands due to a lowering of symmetry from T_d or O_h, respectively, on coordination was detectable either in the solid state or in solution. Raman (Table III) and infrared spectra (Table IV) are consistent with coordination of both phosphorus atoms of the diphosphine as in $(AuX)_2(DPPA)$ and $(AuX)_2(DPPA)_3$. Two structures consistent with the bridging characteristics of III are a binuclear ionic structure (VII) and a polymer ionic formulation (VIII).



VII



VIII

The polymeric structure (VIII) is not favored by the high solubility of both compounds in nonpolar organic solvents. Moreover in dichloromethane the molecular weights of $(AuBF_4)(DPPA)_2$ and $(AuPF_6)(DPPA)_2$ are 1969 and 1846 cm^{-1}, respectively, compared with calculated values of 2143 and 2260 cm^{-1} for the undissociated binuclear species VII. In the polar solvent nitromethane molecular weights are 816 and 935 compared to predicted values of 706 and 723 for fully dissociated 1:2 electrolytes of type VII. These results suggest that in dichloromethane the complexes exist as the ionic binuclear species VII with strong ion paring occurring between cations and anions. In nitromethane the compounds are almost fully dissociated into their constituent ions. In agreement with this, molar conductances in nitromethane are 173.6 and 160.5 ohm^{-1} cm^2 mol^{-1} for $(AuBF_4)_2(DPPA)_4$ and $(AuPF_6)_2(DPPA)_4$, values close to those expected for 1:2 electrolytes in this solvent. It should be noted, however, that molar conductances alone do not distinguish structure VII from VIII because both formulations have the same equivalent weight.[43] Molecular models indicate that with suitable orientation of the phenyl rings, both structures are feasible. Although the data are not conclusive, structure VII appears most likely.

The results presented here together with previous work confirm the varied stereochemistry of gold(I) in complexes with phosphines and arsines. In addition to the better known linear complexes,[33] compounds have now been prepared with planar,[37] tetrahedral,[37,44] and possibly square-pyramidal structures. The unique bridging characteristics of bis(diphenylphosphino)-acetylene are also evident. It is interesting to note that although no gold(I) complexes having two bridging diphosphine ligands were prepared and the only copper(I) complexes of III contain three bridging ligands, reaction of III with nickel carbonyl under mild conditions gives compounds having one, two, and three diphosphine bridges.[45]

The Raman results are particularly interesting in view of the observed shift of $\nu(C{\equiv}C)$ to higher frequency on complexing. In disubstituted acetylenes $\nu(C{\equiv}C)$ appears in the range 2260–2190 cm^{-1}.[46] The value for the C≡C stretching frequency in DPPA is 2097 cm^{-1}, well below the normal range. The low value cannot be due entirely to the inductive effect of the electronegative $P(C_6H_5)_2$ groups as other acetylenes with highly electronegative groups such as CF_3 or $COOCH_3$ absorb in the normal range.[46] It seems likely that this low $\nu(C{\equiv}C)$ frequency is caused, at least in part, by a drift of bonding π-electron density from the acetylenic triple bond to empty $d\pi$ orbitals on phosphorus. $p\pi$–$d\pi$ (C—P) bonding of this type will be facilitated by the linearity of the PCCP system (Figure 1) and by the strongly electron-withdrawing properties of the $P(C_6H_5)_2$ group.[47] Apart from weakening the C≡C bond, an interation of this type will strengthen the adjacent P—C bond. It is interesting therefore that in $P(C{\equiv}CC_6H_5)_3$ the P—C bond length (1.76 Å) is considerably shorter than in triphenylphos-

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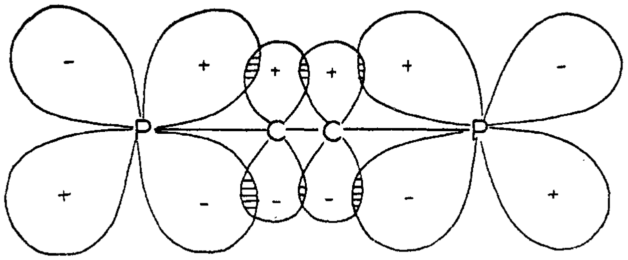

Figure 1.—pπ–dπ (C–P) overlap in the linear skeleton of DPPA.

phine (1.83 Å) and trimethylphosphine (1.85 Å).[24] It should be remembered, however, that while this result may suggest P(dπ)–C(pπ) interaction, a shortening of the P—C bond would be expected since the covalent radius of an sp-hydridized carbon atom is 0.07 Å smaller than that of an sp^3 atom.

If only σ-bonding P→M was important in these copper complexes, a small but noticeable shift to lower frequency of ν(C≡C) would be expected on complexation since σ donation of P→M would effectively increase the electronegativity of the phosphorus atom. Conversely strong dπ–dπ interaction between filled copper dπ orbitals and empty phosphorus dπ orbitals would tend to weaken the interaction pπ–dπ (C–P) and result in a stronger C≡C bond and a consequent high-frequency shift for ν(C≡C).

Extensive M(dπ)–P(dπ) bonding is to be expected with III since preliminary work suggests that this ligand is at least as effective as phosphites in replacing carbon monoxide from metal carbonyls.[45] The Raman results in Table IV confirm this hypothesis. Compounds of the type $(AuX)_2$DPPA show the largest ν(C≡C) shifts in agreement with the fact that only one phosphorus atom per gold atom is available for back-bonding compared with three or four in the remaining complexes. Also, the linear geometry of these species facilitates Au(dπ)→P(dπ) back-bonding. Values for $(AuI)_2(DPPA)_3$ and $(AuNCS)_2(DPPA)_3$ are very close to the range 2120–2125 cm^{-1} for copper(I) complexes of the same type suggesting that Au(I) and Cu(I) have similar π-bonding abilities with phosphorus. As expected the compounds $(AuBF_4)_2(DPPA)_4$ and $(AuPF_6)_2(DPPA)_4$ have the lowest ν(C≡C) frequencies consistent with the presence of four phosphorus π acceptors per gold atom.

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The Interaction of Mercury(II) Salts with Pyridine 1-Oxide

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The interaction of pyridine 1-oxide with mercury(II) salts yields coordination compounds of three different types: $[Hg(C_5H_5NO)_6]A_2$, $[Hg(C_5H_5NO)_2A_2]$, and $[Hg(C_5H_5NO)A_2]_2$. Infrared spectral data, conductivities, and molecular weights indicate that compounds of the type $[Hg(C_5H_5NO)A_2]_2$ are dimeric with pyridine 1-oxide bridging. Compounds of the types $Hg(C_5H_5NO)_6A_2$ and $Hg(C_5H_5NO)_2A_2$ are octahedral. $Hg(C_5H_5NO)_2(CN)_2$ does not appear to fit the above pattern. The type of compound obtained when mercury(II) salts interact with pyridine 1-oxide is determined by the nature of the anion.

Introduction

During recent years pyridine 1-oxide has been found to be a versatile Lewis base, which coordinates through the oxygen atom.[1–6] It has been suggested that pyridine 1-oxide also acts as an excellent π-electron acceptor *via* back-donation,[7,8] although attempts to correlate the strength of the interaction with the π-electron acceptor ability for substituted pyridine 1-oxides were only partially successful. The occurrence of back-donation in these compounds was disputed in recent communications.[9] Also of interest with the coordination compounds of pyridine 1-oxide are its ability to act as a bridging group, exemplified by $[CuA_2(C_5H_5NO)]_2$,[10] and its ability to give complexes

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