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# ORGANOCOPPER(I) COMPLEXES CONTAINING NITROGEN AND PHOSPHORUS BIDENTATE LIGANDS

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## SUMMARY

Some complexes of organocopper(I) compounds with 2,2′-bipyridine, 4,4′-bipyridine, 1,10-phenanthroline, 1,2-bis(diphenylphosphino)ethane and bis(diphenylphosphino) methane have been isolated and characterized. The organocopper(I) complexes of 1,2-bis(diphenylphosphino)ethane reacted with dichloroethane to give vinylchloride and the corresponding copper halide complexes. Some new copper(I) chloride complexes of 1,2-bis(diphenylphosphino)ethane are also reported.

## INTRODUCTION

Several reactions of organocopper compounds useful in organic synthesis have been described in recent years*, but the structures and properties of the compounds have not been investigated in detail. As an extension of our researches on the stabilization of organocopper(I) compounds[2], we prepared some organocopper complexes with the following bidentate ligands: 2,2′-bipyridine (2,2′-Bipy), 4,4′-bipyridine (4,4′-Bipy), 1,10-phenanthroline (Phen), 1,2-bis(diphenylphosphino)ethane (DPPE) and bis(diphenylphosphino)methane (DPPM).

In keeping with the results found with monodentate tertiary arsine[2], attempts to isolate arylcopper complexes of 1,2-bis(diphenylarsino)ethane were unsuccessful.

## RESULTS AND DISCUSSION

### *(I). Organocopper(I) complexes of* 2,2′-*bipyridine,* 4,4′-*bipyridine and* 1,10-*phenanthroline*

Bipy and Phen have been repeatedly used to stabilize organometallic compounds of transition elements. The ligand acts as a bidentate and forms penta-atomic rings with the metal[3]. In contrast, the compounds we obtained by allowing 2,2′-Bipy,

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* See for example ref. 1 and references therein.

4,4′-Bipy and Phen to react with phenylcopper (CuPh), *o*-, *p*-, *m*-tolylcopper (CuT) and *o*-anisylcopper (CuA) are less stable than the parent organocopper compounds, and furthermore also in presence of an excess of the ligand have [Cu]/[L] ratios $\geqslant 2$. (Alkylcopper Phen complexes are likewise unstable[4].)

Analyses and properties of $(\text{Cu-}o\text{-T})_{2.5} \cdot$ 2,2′-Bipy, $(\text{Cu-}p\text{-T})_3 \cdot$ 2,2′-Bipy, $(\text{Cu-}o\text{-T})_4 \cdot$ 4,4′-Bipy, $(\text{Cu-}p\text{-T}) \cdot$ 4,4′-Bipy, $(\text{Cu-}o\text{-T})_2 \cdot$ Phen and $(\text{Cu-}p\text{-T})_2 \cdot$ Phen compounds are summarized in Table 2. Satisfactory analyses could not be obtained for CuPh derivatives owing to their instability, but the course of the reaction and the appearance of the products formed are very similar to those of the Cu-*o*-T complexes. Furthermore [Cu]/[N] ratios about 1.25, 2 and 1 were found for 2,2′-Bipy, 4,4′-Bipy and Phen complexes of CuPh respectively. Preliminary studies of the similarly unstable Cu-*m*-T derivatives showed [Cu]/[N] ratios of 1.5 for 2,2′-Bipy and 1 for Phen complexes. For Cu-*o*-A a larger [Cu]/[N] ratio was observed.

The rates of formation of the complexes were found to depend on the nature of the ligand and on the solvent, decreasing in the order Phen > 2,2′-Bipy > 4,4′-Bipy and tetrahydrofuran ≃ dimethoxyethane > toluene > ether ≫ pentane. The temperature at which reaction starts, depends on the organometallic compound used.

The complexes are sparingly soluble; in the solvents in which they do dissolve, the dissolution seems to be due to a reaction with the solvent. Hydrolysis in moist ether indicates a [Cu]/[Ar] ratio of approximately 1 in all the compounds. Thermal decomposition under nitrogen in anhydrous solvents gives substantial amounts of biaryl derivatives, while decompositon of the solid state gives, copper, biaryl, and free ligand.

IR spectra of the arylcopper complexes were recorded, and, in spite of an unavoidable partial decomposition, reveal a substantial modification of the ligand spectrum.

Probably the organometallic reagent partly retains its polymeric nature, with a chain length depending on the distance of the chelating nitrogen atoms in the ligand. The number *n* of formula units in the chain would be 2 for the Phen compound, with a rigid crystalline structure, while 2,2′-Bipy, in which the two pyridyl groups can rotate about each other, would allow formation of compounds of variable stoichiometry. 4,4′-Bipy, which has the greatest distance between the two nitrogen atoms, would require chains with four units at least. Cage effects can be still present and explain the easy coupling of aromatic radicals in the thermal decomposition of the complexes, as suggested for the starting organometallic compounds.

The complexes formed from *o*-substituted organocopper compounds are, like the parent compounds, less unstable than the other derivatives. A similar effect was observed for aryl complexes of $\text{Fe}^{\text{II}}$, $\text{Co}^{\text{II}}$ and $\text{Ni}^{\text{II}}$ stabilized by tertiary phosphines[5], and was attributed mainly to hindrance by the *o*-substituent to attack on the metal atom.

In order to make a comparison with a π-bonded copper compound, the reactions of (phenylethynyl)copper (CuPE) were studied. No reaction occurred with 2,2′-Bipy or 4,4′-Bipy. With Phen at 0° or higher temperatures the red-brown $(\text{CuPE})_2 \cdot$ Phen was formed (see Table 2). Like the starting compound, this is stable on exposure to air at room temperature. Its IR spectrum is particularly interesting; in keeping with the predictions of Coates and Parkin[6], the C≡C frequency is found at 2040 $\text{cm}^{-1}$, a value intermediate between the C≡C frequency of ligand and uncomplexed (phenylethinyl)copper. There are also, however, two new bands at 1898 and 1884 $cm^{-1}$, whose frequencies seem too low for another type of triple bond.

### (II). *Organocopper(I) complexes of* 1,2-*bis(diphenylphosphino)ethane (DPPE) and bis-(diphenylphosphino)methane (DDPM)*

Under the conditions specified in the experimental section (Table 3), complexes with the following stoichiometry were isolated: $(Cu\text{-}o\text{-}T)_2(DPPE)_3$, $(Cu\text{-}p\text{-}T)_2(DPPE)_3$, $(Cu\text{-}o\text{-}A)_2(DPPE)_3$, $(CuPE)_4(DPPE)_3$, CuPE(DPPE), $(CuPE)_2(DPPE)_3$, $(CuPE)_4(DPPM)_3$. Evidence for the formation of CuPh(DPPE), $(CuPh)_2(DPPE)$ and $(Cu\text{-}p\text{-}T)_2(DPPE)$ complexes was also obtained, but analytically pure compounds could not be isolated. The complexes, in particular those of the (phenylethinyl)copper, are fairly stable to heat and hydrolysis. They are readily soluble in several solvents, but only the CuPE derivatives can be recrystallized unchanged. In keeping with this fact molecular weights in toluene of $(Cu\text{-}o\text{-}T)_2(DPPE)_3$ and $(Cu\text{-}o\text{-}A)_2(DPPE)_3$ gave values lower than expected, confirming that dissociation or reaction had occurred.

The reaction with aliphatic halogenated hydrocarbons is particularly interesting. For example a $(CuAr)_2(DPPE)_3$ complex dissolves completely in dichloroethane (DCE) at room temperature but in a few minutes white crystals precipitate from the dark green-brown solution. At the same time vinyl chloride (identified by GLC and IR) is evolved and free arene is formed in practically stoichiometric yield. [We checked that the arylcoppers did not themselves generate vinyl chloride in DCE. Very small quantities of it were formed from the arylcopper complexes of Bipy and Phen; $(CuPE)_2\cdot$Phen reacted very slowly (involving weeks or by refluxing).] The white crystals were identified as $(CuCl)_2(DPPE)_3(DCE)_2$ identical with authentic samples prepared from CuCl and DPPE in appropriate ratio. Hydrolysis with an ethereal 0.5 *N* HCl solution gave $(CuCl)_2(DPPE)_3$. Similar hydrolysis of the original CuPh complexes gave CuCl(DPPE) and $(CuCl)_2(DPPE)$, illustrating the different stoichiometry of the complexes with DCE.

Unidentified complexes with a higher chlorine content were formed from DPPE derivatives and gaseous HCl. The reactions with bromine and iodine were complicated by oxidation: *e.g.* from $(Cu\text{-}o\text{-}T)_2(DPPE)_3$ with $Br_2$ the complex $CuBr_2(DPPE)O_2$ was isolated.

Complexes isolated from the reaction of arylcopper compounds and DPPM are of different nature and no longer contain the aromatic group bonded to copper.

IR spectra between 1600 and 200 $cm^{-1}$ of some $(CuAr)_2(DPPE)_3$ complexes, including those of the corresponding chlorinated derivative and of the ligand itself, are shown in Fig. 1. While spectra of arylcopper complexes, in which P acts as monodentate ligand[2,7], maintain the characteristics of the uncomplexed reagents, DPPE complexes display a quite different behaviour. Of note are the characteristic features of the spectral regions 900–800, 700–600 and 400–300 $cm^{-1}$, in which the same set of bands is present. Furthermore the P–Ph absorption, at *ca.* 1095 $cm^{-1}$, is shifted to a higher frequency relative to that of ligand and shows an increase in intensity (relative, for example, to adjacent phenyl modes at *ca.* 1025 and 998 $cm^{-1}$). Such facts were suggested by Deacon and Green[8] as criteria for P coordination in complex formation.

IR spectra of CuPE derivatives show strong interactions between metal and acetylenic orbitals in all the complexes, though not as strong as in the CuPE itself.

TABLE 1

INFRARED STRETCHING FREQUENCIES ($\text{cm}^{-1}$) OF THE ACETYLENIC GROUP IN CuPE COMPLEXES

| Compound | $\nu(C{\equiv}C)^a$ |
|---|---|
| CuPE | 1930 |
| $(CuPE)_2Phen$ | 2040 |
| $(CuPE)_4(DPPE)_3$ | 2037 |
| CuPE(DPPE) | 2032 |
| $(CuPE)_2(DPPE)$ | 2057 |
| $(CuPE)_4(DPPM)_3$ | 2023 |

[a] In "nujol" mulls.

Stretching frequencies of the C≡C bond are reported in Table 1. It is to be noted that a single acetylenic band is present and that its intensity decreases with increasing triple bond content. As found for ethynylcopper(I) complexes of monodentate phosphines[6], the absorption frequency does not change significantly with [Cu]/[L] ratio.

## EXPERIMENTAL

Since all the complexes were prepared under nitrogen in anhydrous solvents by rather similar methods, only typical procedures are described. Reaction conditions for individual complexes are specified in Tables 2 and 3, together with some of their properties and analytical data. Preparations of the organocopper compounds have been previously described[9]. Ligands were recrystallized commercial products, and 1,10-phenanthroline was freed from water of crystallization by heating at 100° under vacuum.

IR spectra were recorded as nujol and hostaflon mulls, with a Perkin–Elmer 225 Spectrophotometer. Gases and hydrolysis products were analyzed with a temperature-programmed gas chromatograph, C. Erba Model GT.

### (*I*). *Organocopper*(*I*) *complexes of* 2,2′-*Bipy*, 4,4′-*Bipy and Phen* (*Table* 2)

To an ethereal suspension of the organocopper the ligand was added as a solid (Phen) or ethereal solution. A change in colour immediately occurred. After many hours of stirring the solid was washed with ether until the unreacted ligand was completely removed, then filtered off and dried in a vacuum.

### (*II*). *Organocopper*(*I*) *complexes of DPPE and DPPM* (*Table* 3)

(*a*). *Arylcopper derivatives*. The solid ligand was added to an ethereal suspension of the organocopper at 0° CuT and CuA dissolved in a short time giving yellow solutions, from which a voluminous product slowly precipitated. Dissolution did not occur with CuPh, but there was a slow change in appearance. After many hours of stirring the reaction products were repeatedly washed with ether, filtered and dried in a vacuum.

*Reaction with DCE*. The dried complexes of DPPE were suspended in DCE at 0° and then allowed to reach room temperature. After complete solution white crystals precipitated, which were recrystallized from hot DCE. The same chlorine-

(*continued p.* 257)

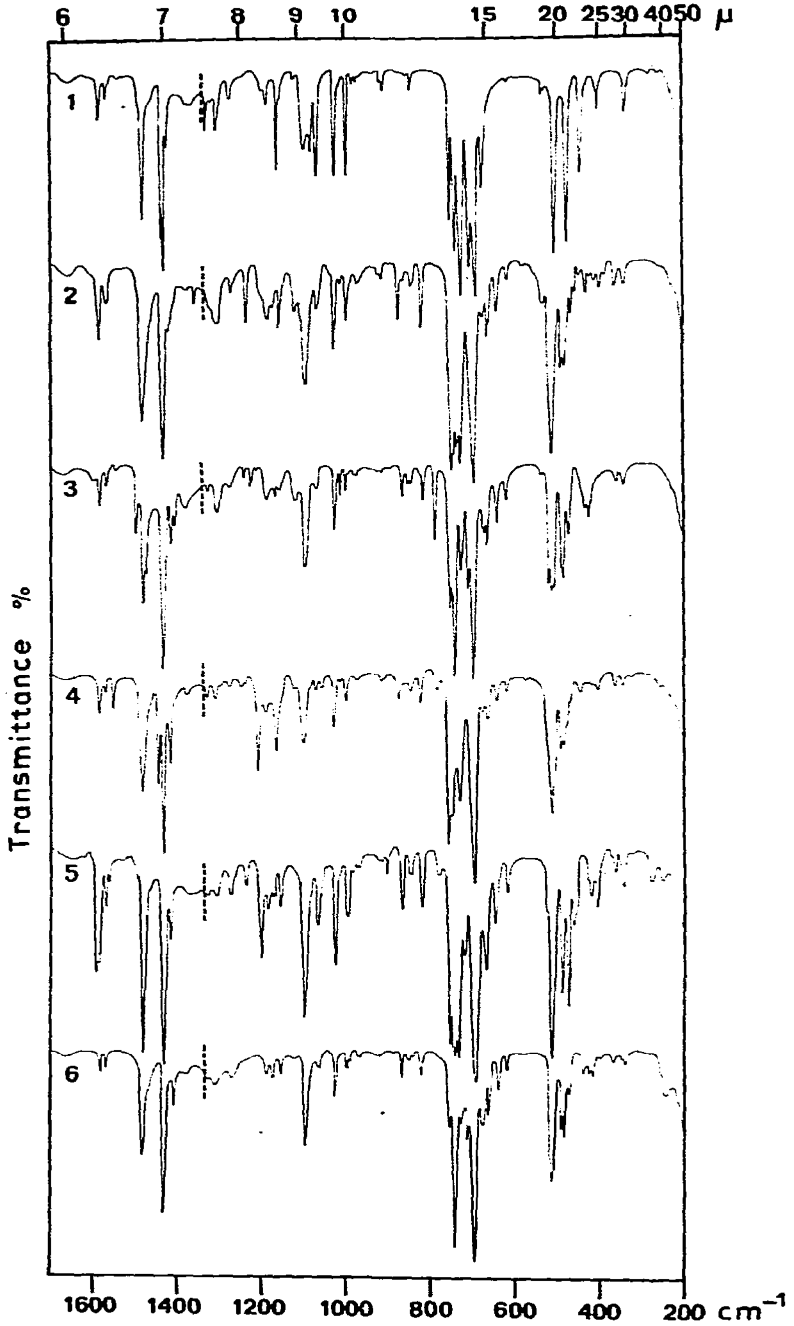

Fig. 1. IR Spectra of some $Cu^I$ complexes of DPPE. 1600–1340 $cm^{-1}$ in hostaflon; 1340–200 $cm^{-1}$ in nujol. (1) DPPE; (2) $(Cu\text{-}o\text{-}T)_2(DPPE)_3$; (3) $(Cu\text{-}p\text{-}T)_2(DPPE)_3$; (4) $(Cu\text{-}o\text{-}A)_2(DPPE)_3$; (5) $(CuPE)_2(DPPE)_3$; (6) $(CuCl)_2(DPPE)_3$.

TABLE 2

ORGANOCOPPER COMPLEXES OF 2,2'-Bipy, 4,4'-Bipy AND Phen

| Complex | Reaction conditions | | | | Analysis (%) | | | Properties of complexes | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | [Cu]/[L] | Solvent | (°C) | (h) | | Found | Calcd. | Colour | M.p. (°C) (under $N_2$) | Stability |
| of CuPh and 2,2'-Bipy | 1 | Ether | −15 | 36 | [Cu]/[N]<br>[Ph]/[Cu] | $\simeq 1.05 \rightarrow 1.25^{b}$<br>$\simeq 1$ | | Brick red | | Stable some hours at 0° under $N_2$; pyrophoric in air |
| of CuPh and 4,4'-Bipy | 1 | Ether | −10 | 18 | [Cu]/[N]<br>[Ph]/[Cu] | $\simeq 2^{b}$<br>$\simeq 1$ | | Dark orange | | Stable some hours at 0° under $N_2$ |
| of CuPh and Phen | 1 | Ether | −20 | 36 | [Cu]/[N]<br>[Ph]/[Cu] | $\simeq 1^{b}$<br>$\simeq 1$ | | Dark red | | Slowly decomposes at 0° under $N_2$; pyrophoric in air |
| $(Cu\text{-}o\text{-}T)_{2.5}\cdot$2,2'-Bipy<br>$C_{27.5}H_{25.5}Cu_{2.5}N_2$ | 1 | Ether | −10 | 10 | C<br>H<br>Cu<br>N<br>[T]/[Cu] | 60.33<br>4.87<br>28.93<br>5.24<br>0.97 | 60.84<br>4.73<br>29.26<br>5.16<br>1.00 | Brick red | >90 dec.$^{c}$ | Stable some hours in dry air at room temperature; immediately decomposes in moist air |
| $(Cu\text{-}o\text{-}T)_4\cdot$4,4'-Bipy<br>$C_{38}H_{36}Cu_4N_2$ | 1 | Ether | −10 | 10 | C<br>H<br>Cu<br>N<br>[T]/[Cu] | 58.25<br>4.61<br>33.12<br>3.69<br>0.97 | 58.90<br>4.68<br>32.80<br>3.62<br>1.00 | Dark orange | >95 dec.$^{c}$ | Stable some hours at room temperature under $N_2$; pyrophoric in air |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $(Cu\text{-}o\text{-}T)_2 \cdot$ Phen | 1 | Ether | 0 | 10 | C | 64.42 | 63.79 | Amaranth | >95 dec.[c] | Stable some hours at room temperature under $N_2$; pyrophoric in air |
| $C_{26}H_{22}Cu_2N_2$ | | | | | H | 4.52 | 4.53 | | | |
| | | | | | Cu | 25.74 | 25.96 | | | |
| | | | | | N | 5.72 | 5.72 | | | |
| | | | | | [T]/[Cu] | 0.94 | 1.00 | | | |
| $(Cu\text{-}p\text{-}T)_3 \cdot$ 2,2′-Bipy | 1 | Ether | −15 | 36 | Cu | 30.47[b] | 30.74 | Deep red brown | >65 dec.[c] | Slowly decomposes at room temperature, rapidly in moist air |
| $C_{31}H_{29}Cu_3N_2$ | | | | | N | 4.47 | 4.52 | | | |
| | | | | | [T]/[Cu] | 0.99 | 1.00 | | | |
| $(Cu\text{-}p\text{-}T)_4 \cdot$ 4,4′-Bipy | 1 | Ether | −10 | 36 | Cu | 31.97[b] | 32.80 | Ochre | | Stable some hours at 0° under $N_2$; pyrophoric in air |
| $C_{38}H_{36}Cu_4N_2$ | | | | | N | 3.49[d] | 3.62 | | | |
| | | | | | [Cu]/[N] | 2.02 | 2.00 | | | |
| | | | | | [T]/[Cu] | 0.96 | 1.00 | | | |
| $(Cu\text{-}p\text{-}T)_2 \cdot$ Phen | 1 | Ether | −15 | 36 | Cu | 26.47[b] | 25.96 | Deep red violet | >80 dec.[c] | Slowly decomposes at room temperature; pyrophoric in air |
| $C_{26}H_{22}Cu_2N_2$ | | | | | N | 5.65 | 5.72 | | | |
| | | | | | [Cu]/[N] | 1.03 | 1.00 | | | |
| $(CuPE)_2 \cdot$ Phen[a] | 1 | Toluene | +60 | 8 | C | 65.52 | 66.00 | Dark red brown | 145–orange<br>>173 dec. | Stable in air at room temperature |
| $C_{28}H_{18}Cu_2N_2$ | | | | | H | 3.51 | 3.56 | | | |
| | | | | | Cu | 25.35 | 24.94 | | | |
| | | | | | N | 5.48 | 5.50 | | | |

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[a] Recrystallized from pyridine and ether. [b] C, H always too low. [c] Largely dependent upon heating rate. [d] Ether present.

TABLE 3

ORGANOCOPPER COMPLEXES OF DPPE AND DPPM

| Complex | Reaction conditions | | | | Analysis (%) | | | Properties of complexes | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | [Cu]/[L] | Solvent | (°C) | (h) | | Found | Calcd. | Colour | M.p. (°C) | Stability |
| $(Cu\text{-}o\text{-}T)_2(DPPE)_3$ | 0.8 | Ether | 0 | 24 | C | 73.0 | 73.44 | Pale cream | 119–121 dec. | Stable in air for some hours at room temperature |
| $C_{92}H_{86}Cu_2P_6$ | | | | | H | 5.73 | 5.76 | | | |
| | | | | | Cu | 8.57 | 8.45 | | | |
| $(Cu\text{-}p\text{-}T)_2(DPPE)_3$ | 0.65 | Ether | 0 | 24 | C[c] | 72.1 | 73.44 | Pale cream | | Slowly decomposes in moist air |
| $C_{92}H_{86}Cu_2P_6$ | | | | | H | 5.72 | 5.76 | | | |
| | | | | | Cu | 8.74 | 8.45 | | | |
| | | | | | P | 12.05 | 12.35 | | | |
| | | | | | [T]/[Cu] | 1.03 | 1.00 | | | |
| $(Cu\text{-}o\text{-}A)_2(DPPE)_3$ | 1 | Ether | 0 | 6 | C | 71.3 | 71.91 | Pale cream | 119–120 dec. | Stable in air for some hours at room temperature |
| $C_{92}H_{86}Cu_2O_2P_6$ | | | | | H | 5.79 | 5.64 | | | |
| | | | | | Cu | 8.20 | 8.27 | | | |
| | | | | | P | 12.35 | 12.10 | | | |
| | | | | | [A]/[Cu] | 0.98 | 1.00 | | | |
| $(CuPE)_4(DPPE)_3$[a,b] | 2 | Toluene | Reflux | 1 | C | 70.9 | 71.26 | Lemon yellow | 229–233 | Stable in air at room temperature |
| $C_{110}H_{92}Cu_4P_6$ | | | | | H | 4.91 | 5.00 | | | |
| | | | | | Cu | 13.60 | 13.71 | | | |
| CuPE(DPPE)[a] | 1 | Toluene | Reflux | 1 | C | 72.5 | 72.52 | Almost white | 215→yellow 219–221 | Stable in air at room temperature |
| $C_{34}H_{29}CuP_2$ | | | | | H | 5.32 | 5.19 | | | |
| | | | | | Cu | 11.34 | 11.28 | | | |
| $(CuPE)_2(DPPE)_3$[a] | 0.66 | Toluene | Reflux | 1 | C | 74.1 | 74.05 | White | 201→yellow 205–208 | Stable in air at room temperature |
| $C_{94}H_{82}Cu_2P_6$ | | | | | H | 5.42 | 5.42 | | | |
| | | | | | Cu | 8.16 | 8.34 | | | |
| $(CuPE)_4(DPPM)_3$[a] | 1.5 | Toluene | 60 | 1 | C | 71.0 | 70.93 | Pale yellow | 154→yellow 161–163 | Stable in air at room temperature |
| $C_{107}H_{86}Cu_4P_6$ | | | | | H | 4.73 | 4.75 | | | |
| | | | | | Cu | 14.08 | 14.03 | | | |

[a] Recrystallized from hot toluene. [b] CuPE(DPPE) crystallizes from the concentrated mother liquor. [c] The compound contains a small quantity of solvent and probably some $(Cu\text{-}p\text{-}T)_2(DPPE)$.

containing complex was obtained from the various different arylcopper derivatives. Its IR spectrum and analysis were in good agreement with the formula $(CuCl)_2(DPPE)_3(DCE)_2$*, *e.g.* from $(Cu\text{-}p\text{-}T)_2(DPPE)_3$. (Found: C, 61.4; H, 4.93; Cl, 13.3; Cu, 7.98. $C_{82}H_{80}Cl_6Cu_2P_6$ calcd.: C, 61.89; H, 5.07; Cl, 13.37; Cu, 7.99%.)

*Reaction with HCl.* To an ethereal suspension of the complex, concentrated HCl was added to give a 0.5 *N* HCl solution, in an amount sufficient to exceed stoichiometric requirements. A white product immediately formed, and after some hours at room temperature this was filtered off, washed thoroughly with ether and dried in a vacuum. The analysis was consistent with the formula $(CuCl)_2(DPPE)_3$ [or CuCl(DPPE) starting from the CuPh complex]. The identity of the products was confirmed by IR spectra and m.p.**, *e.g.* from $(Cu\text{-}o\text{-}T)_2(DPPE)_3$ (Found: C, 67.5; H, 5.13; Cl, 5.5; Cu, 9.09. $C_{76}H_{72}Cl_2Cu_2P_6$ calcd.: C, 67.24; H, 5.21; Cl, 5.09; Cu, 9.12%.); from rough CuPh(DPPE). (Found: C, 62.7; H, 4.64; Cl, 7.5; Cu, 12.69. $C_{26}H_{24}ClCuP_2$ calcd.: C, 62.78; H, 4.86; Cl, 7.13; Cu, 12.77%.)

(*b*). *(Phenylethynyl)copper(I) derivatives.* CuPE and ligand were allowed to react in hot toluene. From the hot filtered solution DPPE complexes precipitated on cooling overnight. For the DPPM derivative concentration of the mother liquor to a very small volume was necessary. The complexes were recrystallized from hot toluene.

We were unable to obtain complexes with a [Cu]/[P] ratio of 1. From such a ratio of reagents, unreacted CuPE was recovered, and complexes with a [Cu]/[P] ratio of 2/3 and 1/2 were isolated from the solution.

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* This and other CuCl complexes of DPPE and DPPM, which are till now not reported in the literature, were prepared from CuCl and ligands. Details are to be published.

** Following the directions of Cariati and Naldini[10], for preparing the complex $(CuCl\cdot DPPE)_3$, we obtained a compound with a m.p. 299.5–300.5° (lit. 192°). The compound prepared from the organocopper complexes has the same m.p.

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