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Preparation of Copper(I)-Phosphine Complexes Having Cu-N Bonds and Their Reactions with Organic Halides

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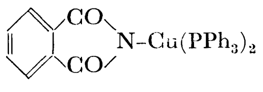
Reactions of a methylcopper complex $CH_3Cu(PPh_3)_2(\text{diethyl ether})_{0.5}$ (PPh_3=triphenylphosphine) with active N-H compounds HNR^1R^2 give the corresponding copper derivatives formulated as $R^1R^2NCu(PPh_3)_n$ ($n=2$ for R^1R^2N=phthalimido, succinimido, *N*-phenylacetamido (**4**), acrylamido, phenylamido, and 2-oxo-1-pyrrolidinyl; $n=1$ for R^1R^2N=acetamido). The IR and NMR spectroscopic data of the complexes support the bonding of the R^1R^2N group to Cu through nitrogen. The reactions of the Cu(I)–N complexes with alkyl and aryl halides (RX) afford the corresponding *N*-substituted compounds RNR^1R^2 in high yields.

Copper and its compounds have been utilized as reagents or catalysts for various organic synthetic reactions such as the Ullmann reaction, Gattermann-Koch reaction, and Sandmeyer reaction.[1)] Although some of the copper-promoted reactions are considered to proceed through the formation of intermediates having Cu–C, Cu–O, or Cu–N bonds, details of the mechanism of the reactions are still vague since chemistry of compounds having Cu–C, Cu–O, or Cu–N bonds has not developed sufficiently. In order to get detailed information concerning the copper-promoted synthetic reactions as well as to develop new copper-promoted synthetic reactions we have prepared Cu(I) complexes having Cu–C,[2)] Cu–O,[3)] or Cu–S[4)] bonds and investigated chemical properties of these complexes. We wish to report on the preparation and properties of Cu(I) complexes having Cu–N bonds. In contrast to bivalent copper complexes for which imido complexes[5a)–5b)] are known since 1905 and the presence of Cu–N covalent bonds in the complexes has been established in some cases by X-ray crystallography,[5b)] only a few reports[6)] have appeared on the preparation of univalent Cu–N complexes, including *in situ* preparation[6b),6c)] of complexes from CuX and R^1R^2NLi. Concerning other transition metal such as Ti, V, and Mo a number of NH_2– or dialkyl- (or diaryl)amido complexes have been prepared and the presence of metal–N covalent bonds has been demonstrated by X-ray crystallography.[7)]

Results and Discussion

Preparation of Complexes. A methylcopper(I) complex $CuCH_3(PPh_3)_2(\text{diethyl ether})_{0.5}$ **1**, convenient starting material reacting with active hydrogen compounds,[3,8)] reacts smoothly at −20 to 0 °C with compounds having active N-H bond including phthalimide, succinimide, acetanilide, acrylamide, acetamide, aniline, and γ-butyrolactam to give complexes having Cu-N bonds with evolution of one equivalent of methane:

$$\underset{\mathbf{1}}{CH_3Cu(PPh_3)_2(Et_2O)_{0.5}} + HNR^1R^2 \rightarrow \underset{\mathbf{2—8}\quad n=1,\,2}{Cu(NR^1R^2)(PPh_3)_n} + CH_4 + 0.5\,Et_2O \qquad (1)$$



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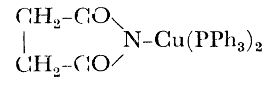

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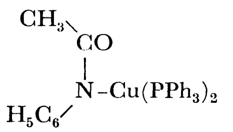

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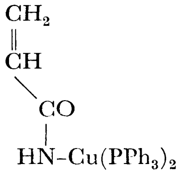

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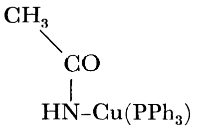

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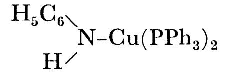

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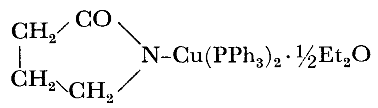

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Generally the reaction with a compound having a more acidic N–H proceeds at a greater rate; the reaction with phthalimide takes only 10 min for completion, that with aniline taking *ca.* 10 h. Compounds with less acidic N–H such as $HN(C_2H_5)_2$ do not react with the methylcopper complex.

Physical properties and analytical data of the complexes are summarized in Table 1. Although most complexes are white, **7** is yellow, showing luminescence sometimes observed in Cu(I) compounds.[9)] The complexes have high thermal stability but undergo gradual decomposition on exposure to the air, the decomposition proceeding much faster in solutions. The low electric conductivity of **2** in acetone excludes the possibility of an ionic structure such as $[Cu(PPh_3)_2]^+[N(CO)_2\text{-}C_6H_4]^-$, suggesting that the imido group is covalently bonded to copper. The phthalimido–copper(I) complex **2** was found to be most stable. It could be prepared also by exchange reactions starting from $ROCu(PPh_3)_n$[3)] or from other complexes **3**—**8** by treatment with 1 equiv of phthalimide to liberate ROH or R^1R^2NH. The number of the triphenylphosphine coordinated to copper can be controlled by the relative acidity of the amido or imido moiety as well as by steric factors. In the more acidic phthalimido (pK_a

TABLE 1. ANALYTICAL DATA OF Cu(I)-N COMPLEXES WITH PPh_3 LIGAND(S)

Complex	Color	Dp.[a] °C	Analysis Found (Calcd), % C	H	N	Cu
2	light green	156—7	72.1 (72.0)	4.6 (4.7)	1.8 (1.9)	8.6 (8.7)
3	white	242—5	70.4 (70.0)	5.3 (5.0)	2.3 (2.0)	
4	white	151	72.7 (73.2)	5.5 (5.3)	2.3 (1.9)	
5	white	83—85	71.2 (71.2)	5.2 (5.2)	2.0 (2.1)	
6	white	172	62.1 (62.5)	5.1 (5.0)	3.8 (3.7)	15.7 (16.6)
7	yellow	69—70	73.8 (74.2)	4.9 (5.3)	2.0 (2.1)	
8	white	110	70.3 (71.1)	5.4 (5.8)	2.1 (2.0)	9.1 (9.0)

a) Decomposition point measured in glass capillaries.

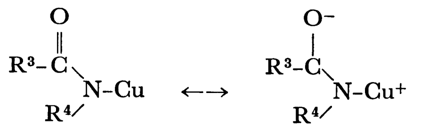
TABLE 2. IR AND NMR SPECTROSCOPIC DATA OF THE Cu(I)-N COMPLEXES WITH PPh_3 LIGAND(S)

Complex	IR (ν/cm^{-1})[a] ν(N-H)	ν(C=O)	$\Delta\nu$(C=O)[c]	^{1}H-NMR (δ/ppm)[b]
2		1650	100	7.4(PPh_3 and $-N(CO)_2C_6H_4$)
3		1610	110	2.44(s, 4H, CH_2), 7.4(m, 30H, PPh_3)
4		1685	−15	2.16(s, 3H), 7.0(m, 23H, *m*, *p*-H of PPh_3 and $C_6\underline{H}_5$-N), 7.6(m, 12H, *o*-H of PPh_3)
5	3270	1640[d] 1540[e]	50[f]	5.2(m, 1H, =CH), 6.1(m, 2H, $=CH_2$), 7.0(m, 19H, *p*-H of PPh_3 and NH), 7.7(m, 12H, *o*-H of PPh_3)
6	3450	1590[d] 1550[e]	80[f]	1.78(s, 3H, CH_3), 7.3(m, 16H, PPh_3 and NH)
7	3400			6.9(m, 5H, C_6H_5-N), 7.0(m, 19H, *m*, *p*-H of PPh_3 and NH), 7.6(m, 12H, *o*-H of PPh_3)
8		1590	100	1.60(q, 8 Hz, 2H, CH_2-C$\underline{H}_2$-CH_2), 2.00(t, 8 Hz, 2H, -CO-$\underline{C}H_2$-), 3.15(t, 7 Hz, 2H, -N-C$\underline{H}_2$-), 7.0(*o*, *p*-H of PPh_3), 7.5(*m*-H of PPh_3)

a) In KBr disk. b) Solvent: C_6D_6 for **3**, **4**, **5**, and **7**; $CDCl_3$ for **2**; CD_2Cl_2 for **6**; toluene-d_8 for **8**. c) $\Delta\nu(C{=}O) = \nu(C{=}O)_{free} - \nu(C{=}O)_{complex}$. d) Amide I; e) Amide II.[13] f) Average of shifts in amide I and amide II bands.

of phthalimido=9.6) and succinimido (pK_a of succinimido=10.5) copper complexes two triphenylphosphine ligands are bonded, while the acetamido (pK_a of acetamido=16) complex contains one triphenylphosphine ligand. The complex containing 2-oxo-1-pyrrolidinyl moiety seems to be situated in the intermediate region; the complex initially formed (complex **8**) has a composition containing two triphenylphosphine ligands. Recrystallization of **8** from toluene gave a complex having one triphenylphosphine ligand based on elemental analysis and NMR data. The value for the carbon content of **8** somewhat lower than the calculated one might be due to the partial dissociation of PPh_3. The triphenylphosphine ligands contained in other bis(triphenylphosphine) complexes are held more firmly.

IR and NMR data of the complexes are summarized in Table 2. The ν(C=C) bands of amides and imides, except for acetanilide, are shifted to lower frequency by 50—110 cm^{-1} on complex formation. The lowering of ν(C=O) frequencies is accounted for by assuming the mixing of the following cannonical structure I and II in the ground state:



$$\underset{\mathrm{I}}{R^3\overset{\overset{O}{\|}}{C}{-}N(R^4){-}Cu} \longleftrightarrow \underset{\mathrm{II}}{R^3\overset{\overset{O^-}{|}}{C}{-}N(R^4){-}Cu^+}$$

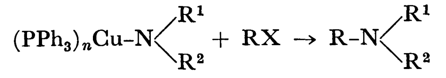
I II

In the cases of phthalimide and succinimide the magnitudes of the shifts are comparable to those observed with Pd and Pt imido complexes which have metal–N

σ-bonds.[10] In contrast to these amido and imido-copper complexes the IR spectrum of the *N*-phenylacetamido complex **4** was somewhat different, the ν(C=O) band being slightly shifted to higher frequency than that of the free acetanilide on complex formation. The reason for this is not clear. However, the IR spectrum may be accounted for by assuming the π-azaallylic type bonding between the *N*-phenyl entity and copper as in benzyl–transition metal complexes.[11]

The NMR spectrum of the succinimido complex **3** shows only one sharp singlet for the CH_2 groups, indicating that the two CH_2 groups are magnetically equivalent in line with the bonding of the succinimido ligand to Cu through nitrogen. The aliphatic C–H signals neighboring the amido group (CH_2 of succinimide, CH_3 of acetamide, and $-NC\underline{H}_2-$ and $-COC\underline{H}_2-$ of γ-butyrolactam) are shifted to higher field by 0.3—0.4 ppm on complex formation. This can be accounted for by the electron migration from Cu to the amido or imido ligands from the discussion on the IR spectra. The electron migration would decrease the an anisotropic paramagnetic effect of the C=O group and increase the diamagnetic shielding of atoms around the –NHCO– bond. A similar upfield shift by 0.4 ppm is observed for α-olefinic hydrogens of acrylamide. In contrast to these amido or imido ligands, no shift of the CH_3 signal in *N*-phenylacetamido is observed on complex formation beyond experimental error. This may be related to the unusual small shift of ν(C=O) to higher frequencies on complex formation.

Reactions with Organic Halides. Reactions of the Cu(I)–N complexes with alkyl or aryl halides lead to the substitution of Cu by the alkyl or aryl group, rendering further evidence for the bonding of the NR^1R^2 moiety to copper through nitrogen:



$$(PPh_3)_nCu-N\begin{matrix}R^1\\R^2\end{matrix} + RX \rightarrow R-N\begin{matrix}R^1\\R^2\end{matrix} \qquad (2)$$

Results of the reactions are summarized in Table 3. The absence of *O*-substituted products excludes the possibility of a structure in which copper is bonded to an oxygen in an enolate form. In the reactions of **2** with aryl halides the yields depend drastically on temperature. For example, the reaction with C_6H_5Br(bp=155 °C) at 140 °C gives only a low yield, whereas that with C_6H_5I(bp=188 °C) or in diglyme (bp=186 °C) at 170 °C gives higher yields. Copper or its compounds are good catalysts for arylation of potassium phthalimide by aryl halides at 155—165 °C, the catalytic reaction being utilized to synthesize aromatic amines.[12] Occurrence of the arylation of **2** with aryl halides gives support to the proposed mechanism[12] involving the formation of a copper phthalimide intermediate during the course of the catalytic reaction.

Reactions of the Cu(I)–N complexes with alkyl halides proceed at much lower temperatures. Complex **2** affords *N*-alkylated phthalimides in almost quantitative yields under mild conditions. Acetyl chloride reacts with **7** to give acetanilide. The same product was obtained also by the reaction of **7** with $(CH_3CO)_2O$ in a 89% yield:

$$\mathbf{7} + CH_3COCl \text{ (or } (CH_3CO)_2O) \rightarrow \underset{89\text{—}92\%}{C_6H_5NHCOCH_3} \qquad (3)$$

Experimental

General. Preparation and recrystallization of copper complexes were carried out under deoxygenated nitrogen or argon or in a vacuum. IR spectra were recorded on a Hitachi Model 295 using KBr discs under nitrogen, NMR spectra on a Japan Electron Optics Lab. JNM-PS-100 spectrometer (TMS as an internal standard). The gas evolved was analyzed with a Hitachi RMU 5B mass-spectrometer and a Shimadzu GC-5B gas chromatograph, its volume being measured with a Toepler pump. Microanalysis of carbon, hydrogen and nitrogen was performed by Mr. T. Saito in our laboratory with a Yanagimoto CHN Autocorder Type MT-2.

Material. $CH_3Cu(PPh_3)_2$(diethyl ether)$_{0.5}$ **1** was prepared as reported previously.[2] Solvents were dried by the usual procedure, distilled, and stored under argon or nitrogen. The N–H compounds were confirmed to be pure by gas chromatography.

Preparation of the Cu(I)–N Complexes. N-*Phthalimidobis(triphenylphosphine)copper(I)* **2**: Diethyl ether (15 cm³) was

Table 3. Reactions of thd Cu(I)–N complexes with organic halides[a]

Complex	Organic halide	Solv.	*T*/°C	*t*/h	Product (% yield/Cu)
2	*p*-$CH_3OC_6H_4Br$	diglyme	170	6	*p*-$CH_3OC_6H_4N(CO)_2C_6H_4$ 84
2	*p*-$CH_3C_6H_4Br$	diglyme	170	6	*p*-$CH_3C_6H_4N(CO)_2C_6H_4$ 48
2	C_6H_5Br	diglyme	170	6	$C_6H_5N(CO)_2C_6H_4$ 64
2	C_6H_5Br	none	140	0.7	$C_6H_5N(CO)_2C_6H_4$ 4
2	C_6H_5I	none	170	1.5	$C_6H_5N(CO)_2C_6H_4$ 46
2	*p*-FC_6H_4Br	diglyme	170	6	*p*-$FC_6H_5N(CO)_2C_6H_4$ 46
2	CH_3I	none	r. t.	3	$CH_3N(CO)_2C_6H_4$ 98
2	$C_6H_5CH_2Br$	none	170	4	$C_6H_5CH_2N(CO)_2C_6H_4$ 95
6	CH_3I	none	r. t.	1	$CH_3CONHCH_3$ 27
7	CH_3I	none	r. t.	5	$C_6H_5NHCH_3$ 24
7	CH_3COCl	none	r. t.	2	$C_6H_5NHCOCH_3$ 92
8	CH_3I	none	0	2	*N*-methyl-γ-butyrolactam 28

a) The reactions were carried out by using 0.15—1.0 mmol of the complex and 1—2 cm³ of the organic halide in 2 cm³ of the solvent.

added to a Schlenk tube containing 670 mg (1.0 mmol) of **1** and 154 mg (1.1 mmol) of phthalimide at −20 °C. Stirring of the mixture for 10 min at −20 °C gave a light green precipitate with evolution of CH_4. Filtration of the solution afforded 680 mg (89%) of the crude product. Recrystallization from acetone yielded light green prisms of **2** (460 mg, 35%). Equivalent conductivity of **2** in acetone at 0 °C was smaller than 1.0 S cm^2.

Succinimidobis(triphenylphosphine)copper(I) **3**: The complex was prepared by the reaction of **1** (750 mg, 1.2 mmol) with succinimide (120 mg, 1.2 mmol) in a similar way to that for the preparation of **2**. The white precipitate obtained was washed with diethyl ether repeatedly and dried in a vacuum to give **3** (600 mg, 74%).

N-*Phenylacetamidobis(triphenylphosphine)copper(I)* **4**: Acetanilide (0.200 g, 1.48 mmol) was added to a Schlenk type flask containing **1** (910 mg, 1.4 mmol) suspended in 5 cm^3 of diethyl ether. The yellow suspension was stirred at 0 °C for 0.5 h in the absence of air to give a white precipitate with evolution of methane (0.97 mol per Cu). The precipitate was crystallized from a mixture of diethyl ether and toluene and dried in a vacuum to give white crystals of **4** (800 mg, 76%).

Acrylamidobis(triphenylphosphine)copper(I) **5**: The complex was prepared by the reaction of **1** (940 mg, 1.5 mmol) with acrylamide (110 mg, 1.5 mmol) in a similar way to that for the preparation of complex **4**. The white precipitate was crystallized from a mixture of diethyl ether and toluene to give white crystals of **5** (810 mg, 83%).

Acetamido(triphenylphosphine)copper(I) **6**: Diethyl ether (15 cm^3) was added to a Schlenk tube containing 1050 mg (1.6 mmol) of **1** and 98 mg (1.7 mmol) of acetamide at −20 °C. Stirring of the mixture for 10 h at 0 °C gave a white precipitate, which was washed with diethyl ether repeatedly and dried in a vacuum to give **6** (610 mg, 97%).

Phenylamidobis(triphenylphosphine)copper(I) **7**: Aniline (150 mg, 1.1 mmol) was added to **1** (670 mg, 1.1 mmol) suspended in 5 cm^3 of diethyl ether. Stirring of the yellow suspension at −10—0 °C for 1 day gave a pale-yellow precipitate, which was washed with diethyl ether repeatedly and dried in vacuum to give **7** (520 mg, 73%).

*(2-Oxo-*1*-pyrrolidinyl)bis(triphenylphosphine)copper(I)* **8**: The complex was prepared by the reaction of **1** (1.6 g, 2.5 mmol) with γ-butyrolactam (0.19 cm^3, 2.5 mmol) in a similar way to that for the preparation of complex **7**. Yield=1.2 g (74%).

Reactions of the Cu(I)–N Complexes with Organic Halides: Bromobenzene (2 cm^3, 19 mmol) and diglyme (2 cm^3) were added to a reaction vessel containing 140 mg (0.19 mmol) of **2**. The mixture was stirred for 6 h under reflux. GLC analysis of the reaction mixture showed formation of 12 mmol (64%) of *N*-phenylphtalimide. The other reactions were carried out in a similar way under conditions given in Table 3.

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