Preparation and Properties of Stable Alkylcopper(I) Complexes Containing Tertiary Phosphine Ligands

Akira MIYASHITA and Akio YAMAMOTO
Tokyo Institute of Technology, Research Laboratory of Resources Utilization
O-okayama, Meguro-ku, Tokyo 152
(Received November 12, 1976)

A variety of stable alkylcopper(I) complexes of composition $RCuL_n$ (n=1—3) containing various monodentate tertiary phosphine ligands (L), such as triphenylphosphine, diphenylmethylphosphine, dimethylphenylphosphine, tributylphosphine, triethylphosphine, and tricyclohexylphosphine have been prepared by the reactions of copper(II) acetylacetonate, dialkylaluminium monoethoxide, and the tertiary phosphines. Similar reactions employing 1,2-bis(diphenylphosphino)ethane(dpe) give $(RCu)_2(dpe)_3$. The complexes have been isolated and characterized by elemental analysis, determination of molecular weight, chemical reactions, IR and NMR spectroscopy. All the isolated complexes show considerable thermal stability compared with alkylcopper compounds without phosphine ligand indicating the marked contribution of these phosphine ligands to the stabilization of the copper-carbon bond. The dpe-coordinated alkylcopper complexes are thermally stable in the solid state but readily decompose in solution with hydrogen abstraction accompanied by scission of the C–P bond of dpe to give Ph_2PCu(dpe), $Ph_2PCH{=}CH_2$, and alkane. These alkylcopper complexes initiate the polymerization of vinyl monomers such as acrylonitrile, methacrylonitrile, methyl acrylate, and methyl methacrylate. Alkyl halides and acyl halides react with the alkylcopper complexes to give cross-coupling products of alkyl groups and alkyl-acyl groups.

The chemistry of organocopper compounds is worthy of study in its own right as a branch of rapidly developing organotransition metal chemistry and also because of its relevance to various copper-catalyzed organic reactions in which organocopper compounds play an important role as reactive intermediates.[1] Many attempts have been made to prepare alkylcopper compounds since the first report by Buckton in 1859.[2] The preparation of methyl- and ethylcopper by the reaction of copper salts with methyllithium,[3a,b] methylmagnesium chloride,[3a] dimethylzinc[4] and tetramethyl- and tetraethyllead[5] has been reported, but most compounds have been prepared *in situ* and attempts to isolate them in the pure state, free from the alkylating agents and reaction by-products, have encountered great difficulties because of their extreme instability which often leads to violent explosions and of their insolubility in common organic solvents.[3–6] The instability of the simple alkylcopper compounds is in contrast to the stability of alkylcopper compounds having electronegative substituents such as fluoroalkylcopper[7] and cyanomethylcopper.[8] Some considerably stable arylcopper complexes are also known.[9]

Employment of ligands such as tertiary phosphines and 2,2′-bipyridine often contributes to the stabilization of alkyltransition metal compounds.[10] Concerning the unsubstituted alkylcopper compounds, however, failure to stabilize the copper-alkyl bond using triphenylphosphine,[11] 2,2′-bipyridine,[4] and *N,N*-dimethylformamide[4] has been claimed. Some alkylcopper complexes coordinated with trimethylphosphite and tributylphosphine have been prepared *in situ* at low temperatures but the complexes have not been isolated in analytically pure state.[3b,12]

We have been able to isolate alkylcopper(I) complexes containing triphenylphosphine[13] and tricyclohexylphosphine[6] by the reactions of bis(acetylacetonato)copper, dialkylaluminium monoethoxide, and the phosphine ligands. Extension of the study to the preparation of other phosphine-containing ligands has revealed the marked stabilizing effect of tertiary phosphine ligands in contrast to statements of some of previous papers and led to the isolation not only of the methylcopper complex but also of series of alkylcopper complexes containing longer alkyl chains which are usually regarded unstable because of their tendency to undergo β-elimination. We now describe the preparation and some properties of these alkylcopper complexes containing various tertiary phosphine ligands. The thermal stability of these complexes will be discussed subsequently.

Results and Discussion

Preparation of the Alkylcopper(I) Complexes Containing Various Monodentate Tertiary Phosphines. The methylcopper(I) complexes having various monodentate tertiary phosphine ligands such as triphenylphosphine (PPh_3), diphenylmethylphosphine(PPh_2Me), dimethylphenylphosphine($PPhMe_2$), tributylphosphine(PBu_3), triethylphosphine(PEt_3), and tricyclohexylphosphine (PCy_3), were prepared from copper bis(acetylacetonate), dimethylaluminium monoethoxide, and the appropriate tertiary phosphine (in a 1 : 4 : 3—4 mole ratio) in diethyl ether or toluene under nitrogen. They were isolated as yellow or light yellow crystals, free from aluminum compounds, after recrystallization from appropriate solvents such as tetrahydrofuran(THF), diethyl ether, toluene or mixture thereof.

$$\left.\begin{array}{l}\mathrm{Cu(acac)_2}\\ \mathrm{Al(CH_3)_2OEt}\\ \text{Tertiary phosphine}\end{array}\right\} \longrightarrow \left[\begin{array}{ll}\mathrm{CH_3Cu(PPh_3)_2(ether)_{0.5}} & \mathbf{1a}\\ \mathrm{CH_3Cu(PPh_3)_3(toluene)} & \mathbf{1b}\\ \mathrm{CH_3Cu(PPh_2Me)_3} & \mathbf{3}\\ \mathrm{CH_3CuPPhMe_2} & \mathbf{4}\\ \mathrm{CH_3CuPEt_3} & \mathbf{5}\\ \mathrm{CH_3CuPBu_3} & \mathbf{6}\end{array}\right.$$

Methylcopper(I) complexes of triphenylphosphine contained toluene or ether as solvent of crystallization. White yellow prisms of $PPhMe_2$, PBu_3, and PEt_3 complexes contained 1—2 molar equivalent of ether or THF as solvent of crystallization which was eliminated by drying *in vacuo*.

Table 1. Analytical data for triphenylphosphine-alkylcopper(I) complexes

No.	Formula	Mp (dec) °C	R/Cu[a)]	[P]/Cu[b)]	Found (Calcd) C%	H%	Cu%
1a	$CH_3Cu(PPh_3)_2(ether)_{0.5}$	75—76	1.01	2.12	72.8 (73.2)	5.8 (6.0)	10.0 (9.9)
1b	$CH_3Cu(PPh_3)_3(toluene)$	70—75	1.02	2.86	77.0 (77.7)	5.8 (5.9)	6.6 (6.6)
1c	$C_2H_5Cu(PPh_3)_2$	56—58	0.97	2.02	72.8 (73.8)	5.5 (5.9)	10.3 (10.3)
1d	$C_2H_5Cu(PPh_3)$	55—58	0.83	0.85	68.1 (67.7)	5.9 (5.7)	19.0 (17.9)
1e	n-$C_3H_7Cu(PPh_3)_2$	61—62	0.98	2.14	74.0 (74.2)	5.8 (5.9)	9.9 (10.1)
1f	i-$C_4H_9Cu(PP_3)_2$	60—63	1.02	1.96	73.9 (74.4)	6.1 (6.0)	10.0 (9.9)

a) Alkyl groups were determined by measuring the amounts of gases evolved after reaction with concd sulfuric acid or decyl alcohol. b) See experimental section. [P] is the amount of coordinated phosphine in the complex.

Table 2. Analytical data for other tertiary phosphine-alkylcopper(I) complexes

No.	Formula	Mp (dec) °C	R/Cu[a)]	[P]/Cu[b)]	Found (Calcd) C%	H%	Cu%
3	$CH_3Cu(PPh_2Me)_3$	95—98	1.01	3.00	71.7 (70.9)	6.9 (6.2)	9.5 (9.4)
4	$CH_3CuPPhMe_2$[c)]	50—51	1.09	0.93	—	—	30.5 (29.3)
5	CH_3CuPEt_3[c)]	40—45	1.12	0.91	—	—	29.0 (29.9)
6	CH_3CuPBu_3[c)]	57—60	1.07	1.14	—	—	23.8 (22.6)
7	i-$C_4H_9CuPCy_3$	100—102	0.98	1.00	65.7 (65.9)	10.2 (10.6)	15.6 (15.8)

a), b) See Table 1. c) Micro analyses were not feasible because of extreme air sensitivity.

The ethyl-, propyl-, isobutylbis(triphenylphosphine)-copper(I) complexes and isobutyl(tricyclohexylphosphine)copper(I) complex were prepared from diethylaluminum ethoxide, dipropylaluminum ethoxide and isobutylaluminum ethoxide, respectively, by a procedure similar to that used for the methyl analogs and were recrystallized from diethyl ether or THF–diethyl ether.

All the isolated complexes are diamagnetic, fairly stable at room temperature in an inert gas atmosphere or *in vacuo* but decomposed rapidly in air. Triphenylphosphine complexes are somewhat light-sensitive and decompose slowly, even at low temperature in sunlight or upon UV irradiation, releasing alkane. Micro analyses of the $PPhMe_2$, PBu_3, and PEt_3 complexes were not feasible because of their extreme instabilities to air. Tables 1 and 2 summarize the analytical data for the isolated alkyl copper complexes having various monodentate tertiary phosphines. Acidolysis or alcoholysis of each alkyl-copper complex released 1 mol equivalent of the corresponding alkane; deuteriolysis with D_2SO_4 liberated alkane-d_1, further supporting the presence of the alkyl-copper bond. These reactions are considered to proceed through stepwise exchange of the acetylacetonato ligands with the alkyl group of AlR_2OEt. Although the nickel[14)] and iron[15)] complexes with alkyl, acetylacetonato, and triphenylphosphine ligands were isolated respectively as intermediates in the alkylation of their acetylacetonates in the presence of triphenylphosphine to give unstable dialkyl complexes, our attempts to isolate alkylcupric complex containing the acetylacetonato ligand were unsuccessful. However, judging from the gas evolved during the reaction, we believe that the intermediate, unstable alkylCu(II) complex is reduced by splitting of the R–Cu bond yielding the alkylCu(I) complexes.

The alkylcopper(I) complexes having various tertiary phosphine ligands have been also prepared by ligand exchanges of triphenylphosphine complexes with more electron-releasing phosphines such as PPh_2Me, $PPhMe_2$, PBu_3, PEt_3, and PCy_3.

$$RCu(PPh_3)_2 + L \xrightarrow[\text{ether}]{} RCuL + 2PPh_3 \quad (2)$$

$$L = PPh_2Me,\ PPhMe,\ PBu_3,\ PEt_3,\ PCy_3$$

In none of these reactions could alkylcopper complexes containing mixed ligands be obtained. Examination of the composition of the alkylcopper complexes in Tables 1 and 2 reveals that the 18 electron rule is fulfilled only for the methylcopper complexes with triphenylphosphine and diphenylmethylphosphine, the least basic ligands among the phosphines used. There seems to be a delicate balance in the number of ligands capable of coordination to copper. Replacement of the methyl group bonded to copper by the ethyl, propyl or isobutyl groups, which are more electron-releasing than methyl, led to alkylcopper complexes containing two triphenylphosphine ligands even when three molar equivalents of phosphine were used. Furthermore, for ethylcopper, when *ca.* 1 mol equivalent of triphenylphosphine was used, a pale grey complex of approximate composition, $EtCu(PPh_3)$, was obtained, which on further addition of 1 mol equivalent of triphenylphosphine was converted into $EtCu(PPh_3)_2$. Replacement of PPh_2Me with the more basic ligand, $PPhMe_2$, caused a decrease in the number of coordinated phosphine ligands from 3 to 1, and coordination of more basic ligands such as PBu_3, PEt_3, and PCy_3 gave only the alkylcopper complex containing one phosphine ligand.

Since some organocopper compounds are known to be aggregated[16] and some of our complexes are coordinatively unsaturated, it was suspected that some might have polymeric structures. Cryoscopic determination of these complexes, however, revealed the complexes to be all monomeric in benzene as shown in Table 3. The molecular weight determination of $CH_3Cu(PPh_3)_2(ether)_{0.5}$ and $CH_3Cu(PPh_3)_3(toluene)$ gave about the half of the calculated values for the compositions indicated, presumably owing to the dissociative removal of the solvents of crystallization and also, in part, of the three triphenylphosphine ligands in benzene solution.

The IR spectra of the alkylcopper complexes showed ν(C–H) bands assigned to the alkyl group bonded to copper at 2980—2750 cm^{-1} and the characteristic absorption bands of coordinated phosphine ligands. The IR spectra of the ν(C–H) bands in the methylcopper complexes appeared at rather low frequencies, (summarized in Table 4) compared with those of the saturated alkanes. A similar trend has been noted also in other methyl-transition metal complexes.[15,17] The medium intensity IR band observed in the methylcopper complexes in the region from 570 to 610 cm^{-1} which decreases on contact with air or upon pyrolysis was tentatively assigned to the ν(Cu–C) band.

TABLE 3. MOLECULAR WEIGHTS OF COPPER-ALKYL COMPLEXES

No.	Formula	Found	Required
1c	$C_2H_5Cu(PPh_3)_2$	633 (±10)	617
1e	$n\text{-}C_3H_7Cu(PPh_3)_2$	544	631
1f	$i\text{-}C_4H_9Cu(PPh_3)_2$	663	645
3	$CH_3Cu(PPh_2Me)_3$	676	679
7	$i\text{-}C_4H_9CuPCy_3$	395	401

Cryoscopic determination in benzene solution.

The ^1H-NMR spectra of the methylcopper complexes showed a singlet due to the methyl group bonded to copper (Table 4). This band was observed as a somewhat broadened singlet but no splitting due to coupling with ^{31}P and ^{65}Cu or ^{63}Cu was observed at the temperature above −30 °C.

The NMR spectrum of the ethyl complex, **1c**, in toluene-d_8 at −20 °C showed a broad unresolved methyl peak at τ 8.90 and a methylene peak at 8.60. The propyl complex **1e** showed broad peaks due to the methyl and the copper-bonded methylene groups at τ 8.95 (5H) and a peak due to the central methylene at 8.60 (2H). In toluene-d_8 at 25 °C the spectrum of $i\text{-}C_4H_9Cu(PPh_3)_2$, **1f**, showed a doublet at τ 9.13 (2H, $C\underline{H}_2$–Cu, $^3J_{H-H}$ 7 Hz), a doublet at 8.68 (6H, $2C\underline{H}_3$, $^3J_{H-H}$ 6 Hz) and an unresolved multiplet at 8.00 (1H, $C\underline{H}$). It is note-worthy that the protons attached to carbon bonded to copper appear at considerably higher field because of the shielding effect of copper in the complexes. It appears that peaks of methyl protons in copper complexes coordinated to rather basic ligands is slightly shifted to higher field, but the effect is not particulary conspicuous.

The ^1H-decoupled ^{31}P NMR spectrum of **3** in toluene at −80 °C showed a sharp singlet resonance at 6.1 ppm (up-field from the external PPh_3 reference in toluene) and a small signal of free PPh_2Me at 19.3 ppm whereas at −40 °C the singlet at 6.1 ppm broadened and shifted to higher field 8.4 ppm accompanied by disappearance of the free PPh_2Me signal. The spectrum of a toluene solution of **3** containing three mol equivalents of added PPh_2Me at −80 °C exhibited a somewhat broadened singlet at 9.2 ppm and a sharp singlet due to free PPh_2Me at 19.7 ppm. At −20 °C the two peaks collapsed to a broadened singlet centered at 16.8 ppm. These results indicate that at −80 °C the methylcopper complex with three PPh_2Me ligands is not extensively

TABLE 4. IR[a] AND NMR[b] SPECTRA OF METHYLCOPPER(I) COMPLEXES

No.	Formula	IR ν(C–H) in alkyl group		IR $\nu(Cu\text{–}CH_3)$	NMR[b] Methyl-Cu signal $\tau_{Cu\text{-}CH_3}$
1a	$CH_3Cu(PPh_3)_2(ether)_{0.5}$	2830 m	2790 s	612 m	10.3
1b	$CH_3Cu(PPh_3)_3(toluene)$	2830 m	2780 s	603 m	10.4
3	$CH_3Cu(PPh_2Me)_3$	2940 m	2770 s	590 m	10.5
4	$CH_3CuPPhMe_2$	2825 m	2775 s	560 w	10.1
5	CH_3CuPEt_3	2830 m	2770 m	575 m	10.3
6	CH_3CuPBu_3	2830 m	2770 m	575 m	10.5
2a	$(CH_3)_4CuAl_2(dpe)_2(OEt)_2$	2970 m, 2920 m, 2875 m 2820 s		615 m	9.84[c]
2b	$(CH_3Cu)_2(dpe)_3$	2820 m	2775 s	596 m, 615 m, 640 m	—
	CH_3CuPCy_3[d]	2820 m	2770 w	568 m	10.5

a) KBr disk; s, strong; m, medium; w, weak; frequencies in cm^{-1}. b) Toluene-d_8 10% solution, toluene-d_8 impurities as internal standard, at room temperature, all singlet signals. c) THF-d_8 15% solution, TMS internal standard. d) See Ref. 6.

dissociated but that upon raising the temperature the complex liberates part of the coordinated PPh_2Me ligands. In the presence of added PPh_2Me at -20 °C the exchange between the coordinated and added PPh_2Me ligands is considered to be taking place rapidly.

Preparation of the Alkylcopper(I) Complexes Containing a Bidentate Tertiary Phosphine. The alkylcopper complexes containing a coordinated bidentate ligand, dpe, present unique features quite different from those of the alkylcopper complexes containing monodentate ligands. Ethyl, propyl, and isobutylcopper complexes of composition $(RCu)_2(dpe)_3$ have been obtained by the reaction of bis(acetylacetonato)copper, dpe and dialkylalminium monoethoxides in diethyl ether or in toluene under nitrogen. Analytical data are given in Table 5.

$$\left.\begin{array}{l} Cu(acac)_2 \\ Ph_2PCH_2CH_2PPh_2(dpe) \\ AlR_2(OEt) \end{array}\right\} \longrightarrow (RCu)_2(dpe)_3 \qquad (3)$$

$$\textbf{2c},\ R=C_2H_5;\ \textbf{2d},\ R=C_3H_7;\ \textbf{2e},\ R=i\text{-}C_4H_9$$

The number of alkyl groups and dpe ligands attached to copper has been determined by elemental analysis, volumetry after acidolysis or alcoholysis, and spectroscopic determination of the released dpe ligands upon acidolysis. Copper complexes having dpe ligands in a Cu/P ratio of 2/3 are known for the arylcopper(I)[18] and copper(I) halide complexes[19] and the molecular structure,[20] in which dpe ligands are bonded with copper, one forming a chelate and the other bridging between copper atoms has been established. The present alkyl complexes with dpe ligands may well have a similar structure, but the instability of the complexes in solution (*vide infra*) has precluded further characterization.

The use of dimethylaluminium monoethoxide in the reaction with $Cu(acac)_2$ and dpe gave a binary complex which is thermally very stable and moderately insensitive to air. The complex contains both copper and aluminum in a ratio of 1 : 2 and four methyl groups per copper, one of which is probably bonded to copper since one mol equivalent of methane was liberated from the complex on thermolysis at 180 °C. On treatment with HCl in diethyl ether, a quantitative yield of ethyl alcohol was obtained. The overall complex compos-i tion is $CuAl_2(CH_3)_4(dpe)_2(OEt)_2$ **2a**. Similar binary addition products containing alkylaluminium components are known for manganese[21] and titanium.[22]

Recrystallization of this complex **2a** from relatively basic solvents such as tetrahydrofuran led to dissociation of the aluminium and copper components and gave a cream yellow complex $(CH_3Cu)_2(dpe)_3$, **2b**. Use of more basic solvents such as pyridine and *N,N*-dimethylformamide led to decomposition of the methylcopper complex liberating CH_4.

Intramolecular Reaction of Alkylcopper Complexes with dpe Ligands Involving the P–C Bond Cleavage of the dpe Ligand. Despite the fact that the dpe-coordinated complexes show substantially enhanced thermal stability in the solid state, dissolution of $(RCu)_2(dpe)_3$ type complexes **2b**—**2e** in THF, benzene, toluene, and pyridine, leads to a quite facile decomposition with the evolution of an almost quantitative amount of alkane as expressed by the following equation.

$$\underset{\textbf{(2b—2d)}}{(RCu)_2(dpe)_3} \xrightarrow[\text{solvent}]{} \underset{\textbf{(2f)}}{Ph_2PCu(dpe)}$$

$$+\ Ph_2PCH{=}CH_2 + RH + [RCu(dpe)] \qquad (4)$$

$$R=CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ i\text{-}C_4H_9$$

The greenish yellow complex **2f** isolated from the reaction solution analyzed as $Ph_2PCu(dpe)$ (Table 5) and gas chromatographic analysis of the reaction products confirmed the formation of diphenylvinylphosphine and of alkanes. Complex **2f** was characterized by its reaction with dry hydrogen chloride yielding diphenylphosphine, PPh_2H, and with methyl iodide or ethyl iodide affording PPh_2Me or PPh_2Et.

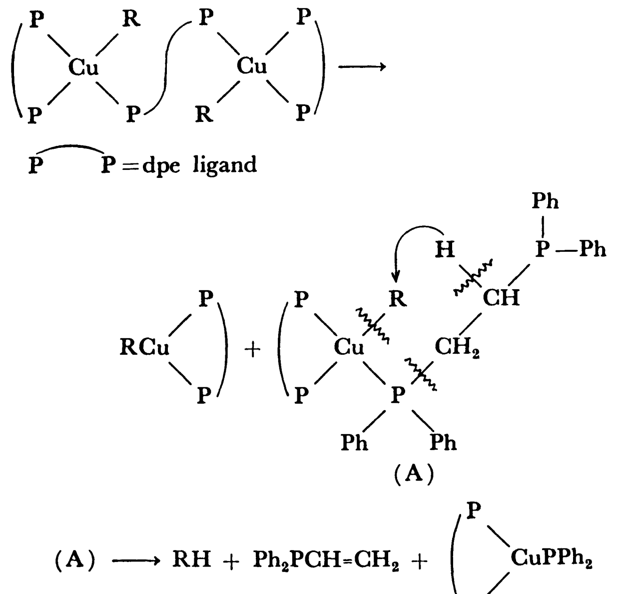
The reaction may proceed as shown in the following Scheme 1.

Dissolution of the coordinatively saturated binuclear complex $(RCu)_2(dpe)_3$ may cause dissociation to RCu-(dpe) and complex (A) containing one chelated dpe ligand and the other dpe ligand bonded to copper as a monodentate ligand having the other phosphine end free in solution. This situation may lead to the approach of one of the methylene groups in the partially dissociated dpe into the proximity of the alkyl group which then attacks the methylene and abstracts hydro-

Table 5. Analytical data for DPE-alkylcopper(I) complexes

No.	Formula	Decomp (mp)°C	R/Cu[a]	[P]/Cu[b]	Found (Calcd) C%	H%	Cu%
2a	$(CH_3)_4CuAl_2(dpe)_2(OEt)_2$	230	4.05	1.88	71.4 (71.4)	6.6 (7.0)	6.4 (6.3)
2b	$(CH_3Cu)_2(dpe)_3$	149—150	1.00	1.53	71.1 (71.0)	6.6 (5.8)	9.2 (9.4)
2c	$(C_2H_5Cu)_2(dpe)_3$	124—127	0.90	1.56	71.4 (71.3)	5.4 (5.9)	8.7 (9.1)
2d	$(n\text{-}C_3H_7Cu)_2(dpe)_3$	130—140	0.98	1.54	72.1 (71.7)	6.6 (6.3)	8.6 (9.0)
2e	$(i\text{-}C_4H_9Cu)_2(dpe)_3$	102—105	1.00	1.51	71.9 (71.9	7.2 (6.4)	9.0 (8.8)
2f	$CuPPh_2(dpe)$	115—116	/	/	70.6 (70.5)	5.6 (5.3)	9.5 (9.8)

a), b) See Table 1.



Scheme 1.

gen, at the same time causing scission of the P–C bond in dpe, thus yielding alkane, diphenylvinylphosphine, and $Ph_2PCu(dpe)$. Addition of one or more equivalent of dpe to the system promoted the reaction: all the alkyl groups were liberated as alkane more rapidly than in the absence of added dpe, and $(RCu)_2(dpe)_3$ was quantitatively converted into $Ph_2PCu(dpe)$, $Ph_2PCH=CH_2$, and the alkane. Presumably the addition of the extra dpe ligand enhances the formation of intermediate species (A) thus promoting decomposition. Addition of Lewis acids such as trimethylaluminium, aluminium trichloride, and boron trifluoride markedly promoted the decomposition even at low temperature. Similar promotion of decomposition of a stable arylcopper complex in the presence of dpe has been reported by van Koten and Noltes.[23]

Attempts to isolate RCu(dpe) using the dpe ligand and $Cu(acac)_2$ (1 : 1 ratio) led to the isolation of an extremely air-sensitive white powder, which could not be identified.

Properties of Alkylcopper Complexes. *Polymerization*: The isolated alkylcopper complexes exhibited polymerization activity toward vinyl monomers containing electron-withdrawing substituents. Acrylonitrile, methacrylonitrile, acrylaldehyde, methyl acrylate, methyl methacrylate, and 2-vinylpyridine were rapidly polymerized in the presence of alkylcopper complexes. As with other alkyltransition metal complexes polymerization mayproceed by a coordination mechanism.[24] Polymerization of vinyl compounds by organocopper complexes has also been reported.[25]

Among the alkylcopper complexes, the binary complex **2a** showed the highest polymerization activity. The polymerization of acrylonitrile, methacrylonitrile, and acrylaldehyde took place explosively, and methyl acrylate and methyl methacrylate also polymerized very rapidly with **2a**. Other dpe-coordinated complexes **2b** and **2c** were also very active, quantitatively converting acrylonitrile, methacrylonitrile, and methyl methacrylate, into their polymers below −10 °C within several minutes.

Reactions with Alkyl and Acyl Halides: Methylcopper complexes **1a**, **1b**, **2b**, and **3** reacted with methyl iodide to yield one mol equivalent of C_2H_6. Reactions with ethyl bromide gave mainly C_3H_8 and small amounts of CH_4, C_2H_4, and C_2H_6. The reactions of the ethylcopper complexes **1c**, **1d**, and **2c** with methyl iodide released only C_3H_8 and propylcopper complexes **1e** and **2d** with methyl iodide liberated only C_4H_{10}. The formation of the cross-coupling products as the main gaseous products and of small amounts of CH_4, C_2H_4, and C_2H_6 in the reaction of the methylcopper complexes with ethyl bromide suggests that an unstable Cu(III) intermediate might be formed by oxidative addition of the alkyl halide to the alkylcopper complexes. Cu(III) complexes have not been isolated, but the comparison of the behavior of the alkylcopper complexes with that of alkylgold complexes, the Au(III) state of which is well known,[26] makes the assumption of the intermediacy of Cu(III) complexes not too unreasonable.

$CH_3Cu(PPh_3)_2(ether)_{0.5}$ **1a** reacted also readily with acetyl chloride to give acetone and with benzoyl chloride to yield acetophenone.

Experimental

Materials and General Procedures. All preparations and recrystallizations were carried out under deoxgenated nitrogen, argon, or *in vacuo*. Solvents were dried by usual procedures, distilled, and stored under argon or nitrogen.

Copper bis(acetylacetonate) was prepared as described in the literature.[27] Found; C, 45.3; H, 5.49; Cu, 24.4%(Calcd for; C, 45.8; H, 5.39; Cu, 24.3%). Dialkylaluminium monoethoxide was prepared by the reaction of trialkylalminium with ethyl alcohol in hexane followed by vaccum distillation.

Triphenylphosphine was used as purchased, mp 80—81 °C. dpe,[28] tricyclohexylphosphine,[29] diphenylmethylphosphine,[30] dimethylphenylphosphine,[28] triethylphosphine,[30] and tributylphosphine[31] were prepared as described in the literature.

Analytical Methods. IR spectra were recorded on a Hitachi Model EPI-G3 using KBr discs prepared under nitrogen and proton NMR spectra were recorded on a Japan Electron Optics Lab. JNM-PS-100 spectrometer. Evolved gases were analyzed using a Hitachi RMU-5B mass-spectrometer and a Shimadzu GC-5B gas chromatograph. Microanalyses for carbon, hydrogen and nitrogen were performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2. Triphenylphosphine and dpe contents were determined spectroscopically after hydrolysis with dilute sulfuric acid or by weighing triphenylphosphine oxide. The tricyclohexylphosphine-content was also determined by weighing its oxide, as described above. The other phosphine contents were determined by NMR proton concentration measurements as compared with internal references in their NMR spectra. Molecular weights were determined in benzene solution by a cryoscopic method.

The copper-content was determined by iodometry after digesting the sample with concentrated sulfuric acid. The aluminium content was determined, after the removal of cupric hydroxide and phosphine, gravimetrically as the alminium oxime complex, $Al(C_9H_6ON)_3$.

Preparation of a Series of Alkylcopper Complexes with Triphenylphosphine. *$CH_3Cu(PPh_3)_2(ether)_{0.5}$, **1a***: To an ethereal suspension of copper bis(acetylacetonate) 2.6 g (10 mmol) and 3 molar eqivalents of triphenylphosphine(7.8 g), 4 molar equivalents of dimethylalminium ethoxide(6.5 ml) was added slowly at -40 °C. The mixture was allowed to react initially at -40 °C and the temperature was subsequently raised gradually to -10 to 0 °C until yellow crystals precipitated from the yellow orange solution. The complex wihch was separated by filtration was dissolced in ether–THF below 0 °C. From the yellow orange solution, the yellow cristals which were obtained upon cooling, were filtered, repeatedly washed with dry ether, dried *in vacuo* at room temperature in the dark and characterized as $CH_3Cu(PPh_3)_2 \cdot (ether)_{0.5}$; yield, 5.5 g (86%). Upon pyrolysis at 85 °C, **1a** gave one half molar equivalent of diethyl ether which was identified by mass spectrometry. The NMR spectrum of **1a** in THF had a singlet at τ 10.3 (3H, $C\underline{H}_3$–Cu), a quartet at 7.5 (2H, $-C\underline{H}_2-$ in ether), a triplet at 8.8 (3H, $C\underline{H}_3-$ in ether) and a multiplet at 2.5 (30H, $C_6\underline{H}_5$).

$CH_3Cu(PPh_3)_3$(toluene), ***1b***: Dimethylalminium ethoxide (5 ml, 30 mmol) was added slowly to an ethereal suspension of copper bis(acetylacetonate) (2.0 g, 7.6 mmol) and PPh_3 (7.3 g, 27 mmol) at -40 °C. The mixture was subsequently raised gradually to room temperature (6 h) to give a deep yellow solution. On cooling, the light yellow needles which precipitated were filtered off and recrystallized from toluene, washed with hexane, dried *in vacuo* and characterized as $CH_3Cu(PPh_3)_3$(toluene); yield, 3.6 g (50%). On pyrolysis at 160 °C, **1b** gave one molar equivalent of toluene. The NMR spectrum of **1b** in THF showed singlets at τ 10.4 (3H, $C\underline{H}_3$–Cu), 7.7 (3H, $C\underline{H}_3-C_6H_5$) and a multiplet at 2.7 (50H, $C_6\underline{H}_5$).

$C_2H_5Cu(PPh_3)_2$, ***1c***: $Cu(acac)_2$ (2.6 g, 10 mmol), PPh_3 (7.8 g, 30 mmol) and diethylalminium ethoxide 7 ml were mixed at -30 °C. The temperature was gradually raised to 0 °C, and a bright yellow complex slowly precipitated with dissolution of $Cu(acac)_2$ in ether. After 7 h stirring the reaction products were removed by filtration, recrystallized from ether–THF, dried *in vacuo* and characterized as C_2H_5-$Cu(PPh_3)_2$; yield, 4.4 g (71%).

$C_2H_5CuPPh_3$, ***1d***: Diethylaluminium monoethoxide (7.0 ml, 45.6 mmol) was added to the ethereal suspension containing $Cu(acac)_2$ (4.0 g, 15.2 mmol) and triphenylphosphine (4.5 g, 17.2 mmol) at -40 °C. From the dark yellow solution, obtained after the $Cu(acac)_2$ had completely dissolved in ether, a white gray complex gradually precipitated as the temperature was raised to 0 °C. After stirring for 3 h below 0 °C, the complex was filtered, washed repeatedly with ether and dried *in vacuo* at room temperature (yield, 60%).

n-*$C_3H_7Cu(PPh_3)_2$*, ***1e***: $Cu(acac)_2$ (2.6 g, 10 mmol), PPh_3 (7.8 g, 30 mmol) and dipropylalminium ethoxide(8 ml) were mixed at -30 °C. The temperature was gradually raised to 0 °C, and an orange yellow solution was obtained with dissolution of $Cu(acac)_2$ in ether. On cooling the solution after addition of a small amount of hexane, greenish yellow prisms precipitated, which were filtered, repeatedly washed with ether–hexane, and dried *in vacuo* at room temperature in the dark. The complex was characterized as *n*-$C_3H_7Cu(PPh_3)_2$; 3.0 g (48%).

i-*$C_4H_9Cu(PPh_3)_2$*, ***1f***: This compound was prepared by the procedure described above. The complex, obtained as primrose-yellow crystals, was characterized as *i*-C_4H_9Cu-$(PPh_3)_2$, (yield, 54%).

Preparation of Alkylcopper Complexes with 1,2-Bis(diphenyl phosphino)ethane. Methylcopper Complex Containing Alkylalminium Components, $CuAl_2(CH_3)_4(dpe)_2(OEt)_2$, ***2a***: Dimethylalminium ethoxide, 10 ml, was added slowly to an ethereal suspension containing copper bis(acetylacetonate) (4.5 g) and dpe (17.1 g) at -40 °C. When the mixture was subsequently raised gradually to room temperature, a cream yellow complex slowly precipitated with dissolution of copper bis(acetylacetonate) in ether. After about 10 h of stirring a light yellow precipitate formed was filtered, repeatedly washed with ether, dried *in vacuo*, and characterized as $CuAl_2(CH_3)_4(dpe)_2(OEt)_2$. The complex was diamagnetic and had the correct elemental analyses, (yield, 80—90%). Acidolysis with dry HCl in ether resulted in a quantitative yield of CH_4 together with ethyl alcohol.

$(CH_3Cu)_2(dpe)_3$, ***2b***: The alminium-containing complex **2a** was dissolved in THF and addition of ether to the resultant light orange solution gave white yellow prisms on cooling overnight. The crystals were filtered, washed repeatedly with ether, dried *in vacuo* and characterized as $(CH_3Cu)_2$-$(dpe)_3$, (yield, 20%).

$(C_2H_5Cu)_2(dpe)_3$, ***2c***: Copper bis(acetylacetonate) (2.6 g) and dpe (8.8 g) were suspended in 100 ml of ether and 6.5 ml of diethylalminium ethoxide was added at -40 °C. The mixture was allowed to react initially at this temperature which was then raised gradually to room temperature until the reagents completely dissolved in ether, and then a lemon yellow complex was gradually precipitated from the resulted yellow orange solution. After about 5 h of stirring at room temperature, the reaction product was filtered, repeatedly washed with ether, dried in vacuum, and characterized as $(C_2H_5Cu)_2(dpe)_3$, (yield, 85%). Attempts of recrystallization resulted in decomposition.

*(*n-*$C_3H_7Cu)_2(dpe)_3$*, ***2d*** *and (*i-*$C_4H_9Cu)_2(dpe)_3$*, ***2e***: These were prepared by the procedure described above but attempts of recrystallization resulted in decomposition, (yield, 80—90%).

$Ph_2PCu(dpe)$, ***2f***: The alkylcopper complexes of dpe, $(CuR)_2(dpe)_3$, were suspended in THF or toluene and then allowed to warm from room temperature until the complexes were completely dissolved in THF or toluene. After cooling the solution, greenish yellow prisms were obtained, which were recrystallized from THF or toluene, (yield, 45%).

Preparation of Alkylcopper(I) Complexes with Other Tertiary Phosphines. $CH_3Cu(PPh_2Me)_3$, ***3***: To an ethereal suspension of $Cu(acac)_2$, 4 molar equivalents of PPh_2Me was added at -45 °C and then 4 molar equiv of Me_2AlOEt was slowly added at the same temperature. Blue crystals of $Cu(acac)_2$ gradually dissolved in ether with evolution of CH_4 and C_2H_6 with temperature being raised gradually to room temperature. A white yellow complex precipitated from the orange yellow solution on stirring for 6 h. The complex which was separated by filtration was dissolved in ether–THF at the temperature below 0 °C. From the yellow solution, white yellow crystals were obtained on cooling, washed repeatedly with ether, dried *in vacuo* at room temperature in the dark and characterized as $CH_3Cu(PPh_2Me)_3$, (yield, 63%). The NMR spectrum of **3**, in toluene-d_8 at -20 °C, had a singlet at τ 10.50 (3H, $C\underline{H}_3$–Cu), a singlet at 8.60 (9H, $C\underline{H}_3$–P), a multiplet at 3.16—2.50 (30H, $(C_6\underline{H}_5)_2$–P).

$CH_3Cu(PPhMe_2)$, ***4***: At -45 °C, 3 molar equivalents of $PPhMe_2$ was added to an ethereal suspension of $Cu(acac)_2$ and then 4 molar equiv of Me_2AlOEt was slowly added. After the temperature was gradually raised to 0 °C with stirring, a light yellow solution was obtained. The solution was allowed to condense by evaporation under a reduced pressure and then a small amount of hexane was added to it. After cooling the solution at -78 °C, white yellow crystals slowly precipitated and were recrystallized from ether–hexane solvent mixture. The white yellow complex thus obtained was characterized as $CH_3CuPPhMe_2$, (yield, 35%).

CH_3CuPBu_3, ***6***: To an ethereal suspension of $Cu(acac)_2$, 3—4 molar equiv of PBu_3 was added at -40 °C and then 4 molar equiv of dimethylalminium ethoxide was slowly added at the same temperature. With a gradual raise of the temperature, $Cu(acac)_2$ dissolved in ether and CH_4 and C_2H_6 were released to give a yellow solution at room temperature. After condensation of the ether solution, the residue was extracted with hexane. White yellow prisms, isolated from the hexane solution upon cooling, were washed repeatedly with small amounts of hexane below 0 °C, dried *in vacuo* and characterized as CH_3CuPBu_3, **6**, (yield 65%).

CH_3CuPEt_3, ***5***: This was prepared by the procedure described above, and recrystallized from an ether–THF–hexane solvent mixture, (yield, 45%). Light yellow crystals.

Preparation of Butyl(tricyclohexylphosphine)copper, ***7***: $Cu(acac)_2$ 4 g (15 mmol) and tricyclohexylphosphine 9 g (31.9 mmol) were suspended in 100 ml of ether, and 13 ml of diisobutylaluminium ethoxide was added to the suspension at -30 °C. After the temperature was raised gradually to room temperature with stirring, a pale yellow solution was obtained. After cooling the solution, cream yellow prisms deposited, which were filtered, washed repeatedly with ether and hexane, dried *in vacuo*, and characterized as i-$BuCuPCy_3$. The complex was recrystallized from ether, (yield, 60%).

Polymerization. Most of the polymerizations were carried out in a sealed ampoule or in a Schlenk type flask in which the alkylcopper complex (50—100 mg) and olefin (5—10 ml) were transferred in an atmosphere of nitrogen or by a trap-to-trap distillation *in vacuo*. After the polymerization was complete, the content in the flask was poured into acidic methanol. The precipitate was filtered, washed with methanol and dried. The polymers of acrylonitrile obtained with **1a** and **1c** had molecular weights of *ca.* 1.2×10^4, and poly(methyl methacrylate) $1.3—7.1\times10^5$ determined by a viscosity method.

References

1) (a) R. G. R. Bacon and H. O. Hill, *Quart. Rev.*, **19**, 95 (1965); (b) J. F. Normant, *Synthesis*, **1972**, 63; (c) T. Saegusa, T. Tsuda, and Y. Ito, *Kogyo Kagaku Zasshi*, **72**, 1627 (1969); (d) T. Saegusa and Y. Ito, *Kagaku no Ryoiki, Special Issue*, No. 89, 157 (1970); (e) T. Saegusa and Y. Ito, *Synthesis*, **1975**, 291.

2) G. Buckton, *Ann. Chem.*, **109**, 225 (1859).

3) (a) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952); (b) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Am. Chem. Soc.*, **31**, 3128 (1966).

4) K. H. Thiele and J. Kölher, *J. Organomet. Chem.*, **12**, 225 (1968).

5) (a) H. Gilman and L. A. Woods, *J. Am. Chem. Soc.*, **65**, 435 (1943); (b) G. Costa, G. De Alti, L. Stefani, and G. Boscarato, *Ann. Chim.*, **52**, 289 (1962); (c) C. E. H. Bawn and F. H. Whitby, *J. Chem. Soc.*, **1960**, 3926, 4162.

6) T. Ikariya and A. Yamamoto, *J. Organometal. Chem.*, **72**, 145 (1974).

7) (a) J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *Chem. Commun.*, **1967**, 1259; (b) J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *J. Chem. Soc., Perkin Trans. 1*, **5**, 639 (1972); (c) V. C. Macloughlin and J. Thrower, *Tetrahedron*, **25**, 592 (1969).

8) T. Tsuda, T. Nakatsuka, T. Hirayama, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, **1974**, 557.

9) (a) G. Costa, A. Camus, L. Gatti, and N. Marsich, *J. Organomet. Chem.*, **5**, 568 (1966); (b) G. Costa, A. Camus, N. Marsich, and L. Gatti, *J. Organomet. Chem.*, **8**, 339 (1967); (c) G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, **84**, 117, 129, 419 (1975) and references cited therein.

10) For example, M. L. H. Green, "Organometallic Compounds," Vol. 2, Methuen, London (1968).

11) G. Costa, G. Pellizer, and F. Rubessa, *J. Inorg. Nucl. Chem.*, **26**, 961 (1964).

12) (a) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **33**, 949 (1968); (b) G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Am. Chem. Soc.*, **94**, 232 (1972); (c) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *J. Am. Chem. Soc.*, **92**, 1426 (1970).

13) A. Yamamoto, A. Miyashita, T. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **45**, 1583 (1972).

14) (a) P. W. Jolly, K. Jonas, C. Krüger, and T. H. Tsay, *J. Organomet. Chem.*, **33**, 109 (1971); (b) A. Yamamoto, T. Yamamoto, T. Saruyama, and Y. Nakamura, *J. Am. Chem. Soc.*, **95**, 4073 (1973); T. Yamamoto, T. Saruyama, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 589 (1976).

15) Y. Kubo and A. Yamamoto, *J. Organomet. Chem.*, **46**, C50 (1972); *ibid.*, **84**, 369 (1975).

16) (a) A. Cairncross and W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 248 (1971); (b) M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972); (c) G. van Koten and J. G. Noltes, *J. Chem. Commun.*, **1970**, 1107; (d) J. M. Guss, R. Mason, and K. M. Thomas, *J. Organomet. Chem.*, **40**, C79 (1972).

17) (a) L. Dahlenburg and R. Nast, *J. Organomet. Chem.*, **71**, C49 (1974); (b) D. M. Adams, *J. Chem. Soc.*, **1962**, 1220.

18) A. Camus and N. Marsich, *J. Organomet. Chem.*, **21**, 249 (1970).

19) N. Marsich, A. Camus, and E. Cebulec, *J. Inorg. Nucl. Chem.*, **34**, 933 (1972).

20) V. G. Albano, P. L. Bellon, and G. Ciano, *J. Chem. Soc., Dalton Trans.*, **1972**, 1938.

21) A. Yamamoto, K. Kato, and S. Ikeda, *J. Organomet. Chem.*, **60**, 139 (1973).

22) A. Yamamoto, T. Murai, E. Ooshima, and S. Ikeda, unpublished.

23) G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, **1972**, 452.
They have confirmed the dimeric structure for $Ph_2PCu(dpe)$, private communication.

24) (a) A. Yamamoto and S. Ikeda, Progress in Polymer Science Japan, Vol. 3, 49, ed by S. Okamura and M. Takayanagi, Kodansha, Tokyo (1972); (b) T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **45**, 1111 (1972); (c) Y. Kubo, A. Yamamoto, and S. Ikeda, *ibid.*, **47**, 393 (1974); (d) S. Komiya, A. Yamamoto, and S. Ikeda, *ibid.*, **48**, 101 (1975); (e) A. Yamamoto, *Ann. N.Y. Acad. Sci.*, **239**, 60 (1974); A. Yamamoto and S. Ikeda, *J. Macromol. Sci. Chem.*, **A9**, 931 (1975).

25) T. Saegusa, S. Horiguchi, and T. Tsuda, *Macromolecules*, **8**, 112 (1975).

26) A. Tamaki and J. K. Kochi, *J. Organomet. Chem.*, **40**, C81 (1972).

27) M. M. Jones, *J. Am. Chem. Soc.*, **71**, 3188 (1959).

28) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

29) W. H. Gruber and J. Ellermann, *Chem. Ber.*, **23**, 1307 (1968).

30) J. A. C. Allison and F. G. Mann, *J. Chem. Soc.*, **1949**, 2915.

31) M. J. Mays and S. M. Pearson, *J. Chem. Soc., A*, **1968**, 2281.