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Mono- and dinuclear alkoxide copper complexes with PPh_3 ligands

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Abstract

Methylcopper complex, $CuMe(PPh_3)_2(Et_2O)_{0.5}$ (**1**), reacts with $HOCH(CF_3)_2$ to give $Cu(OCH(CF_3)_2)(PPh_3)_3$ (**2a**). Similar reactions of **1** with $HOCHPh_2$ give $Cu(OCHPh_2)(PPh_3)_3$ (**3a**) or $Cu(OCHPh_2)(PPh_3)_2$ (**3b**) depending on the reaction conditions. Reaction of **1** and phenol with addition of PPh_3 gives $Cu(OPh)(PPh_3)_3$ (**4a**). The ^1H NMR spectra and results of elemental analyses of **2a**, **3a**, **3b**, and **4a** agree well with the proposed formula. Complex **2a** crystallizes in the orthorhombic space group $Pn2_1a$, with $a = 18.804(2)$ Å, $b = 19.655(4)$ Å, $c = 13.175(3)$ Å, $Z = 4$, and $V = 4869$ Å^3. The Cu center is in pseudotetrahedral coordination with the Cu–O distance of 2.087(6) Å. Phenoxide copper complex, $Cu(OPh)(PPh_3)_2$ (**4b**), which is prepared from the already reported reaction of **1** with phenol, crystallizes in the monoclinic space group $P2$, with $a = 13.955(3)$ Å, $b = 17.610(3)$ Å, $c = 13.961(3)$ Å, $\beta = 90.06(2)°$, $Z = 2$, and $V = 3430$ Å^3. The molecule has a dinuclear structure in which two pseudotetrahedral Cu centers are bridged by two μ^2-phenoxide ligands. Complex **3a** reacts with $HOCH(CF_3)_2$ to give **2a**, while reactions of the fluoro alcohol with **3b** give **2a** or $Cu(OCH(CF_3)_2)(PPh_3)_2$ (**2b**) depending on the conditions. Reaction of $HOCHPh_2$ with **2a** does not cause the alkoxide ligand exchange. Complex **2a** reacts with phenol and with phenyl acetate to give **4b** in high yields, while **4b** does not undergo exchange of the phenoxide ligand by $HOCH(CF_3)_2$. Reaction of **3a** with 1,4-diethynylbenzene gives a copper complex formulated as $(Ph_3P)Cu(C{\equiv}CC_6H_4C{\equiv}C)Cu(PPh_3)$ (**5**). The PEt_3 coordinated complex $(Et_3P)Cu(C{\equiv}CC_6H_4C{\equiv}C)Cu(PEt_3)$ (**6**) is prepared by reaction of PEt_3 with **5**.

Key words: Copper; Alkoxide; Hydrogen bonding; Crystal structure

1. Introduction

Copper(I) alkoxides, $[Cu(OR)]_n$, have been reported to promote synthetic organic reactions such as coupling of the alkoxide ligand with organic halides to give the corresponding ethers [1,2] and cross coupling of iodoarene with propiolic acid [3]. Cu^{II} alkoxides promote dimerization of phenyl acetylene to give diphenyl diacetylene [4]. Organocuprates having an alkoxide ligand also promote various coupling reactions where the alkoxide group plays an important role as the supporting ligand [5]. Previously alkoxide copper(I) complexes with PPh_3 ligands, $Cu(OR)(PPh_3)_n$ (R = Me, Et, Pr, and Ph *etc.*; $n = 1, 2$), have been prepared by reactions of the alcohols with $CuMe(PPh_3)_m$ [6]. The complexes react with carboxylic esters and with alkyl halides to give the corresponding esters and ethers, respectively, through coupling of the alkoxide ligand with acyl or alkyl group of the substrates. Reactions of CO_2 with the complexes give several copper complexes containing carbonato or hydrogencarbonato ligands. Although the above alkoxide copper complexes with PPh_3 ligands show interesting chemical properties, detailed coordination structures have not been elucidated. Similar copper alkoxides with electron withdrawing substituents such as CF_3 and Ph groups in the alkoxide ligands would have more stable Cu–O bond than the above already reported alkoxide complexes and would be suitable for preparation of the single crystals for X-ray analyses and for determination of the structures in solutions by spectroscopic measurement. The fluoro alkoxide complexes of Group 8–10 metals were reported to have much higher stability than the corresponding methoxide and ethoxide complexes [7–10] and have a tendency to form mononuclear structure rather than di- or multinuclear structures with bridging alkoxide ligands. Here we report preparation of cop-

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TABLE 1. ^1H NMR data of the complexes **2a**, **2b**, **3a**, **3b** and **4a** [a]

Complex	$P(C_6H_5)_3$ [c]	OC*H*	OC_6H_5
2a	7.0–7.5 (m, 45H)	4.34 (sep, 1H) [b]	–
2b	7.0–7.5 (m, 30H)	4.34 (sep, 1H) [b]	–
3a	7.2–7.6 (m, 55H)	5.84 (s, 1H)	–
3b	7.2–7.5 (m, 40H)	5.84 (s, 1H)	–
4a	7.1–7.5 (m, 46H) [d]	–	6.3–6.8 (m, 4H) [d]

[a] δ values obtained from measurement in CD_2Cl_2 at 25°C.
[b] $J(H-F) = 7$ Hz.
[c] The peaks of **3a** and **3b** include the peak due to phenyl hydrogens of the $OCHPh_2$ ligand.
[d] The *p*-hydrogen of the phenoxide ligand is overlapped with the peaks due to PPh_3 hydrogens.

per(I) complexes with CF_3 or Ph substituted alkoxide ligands as well as the results of crystallography and study on the chemical properties.

2. Results

2.1. Preparation and characterization of $Cu(OR)(PPh_3)_n$ ($R = CH(CF_3)_2$, $CHPh_2$)

Reaction of $CuMe(PPh_3)_2(Et_2O)_{0.5}$ (**1**) with $HOCH(CF_3)_2$ gives $Cu(OCH(CF_3)_2)(PPh_3)_3$ (**2a**) as a white solid in a 30% yield. The reaction with addition of PPh_3 to the reaction mixture also causes formation of **2a** which is isolated in a higher yield (68%).

$$\underset{\mathbf{1}}{(Ph_3P)_2Cu{-}Me} + HOCH(CF_3)_2 \; (+ PPh_3) \xrightarrow{-CH_4} \underset{\mathbf{2a}}{(Ph_3P)_3Cu{-}OCH(CF_3)_2}$$

The reactions both with and without PPh_3 addition give **2a** as the sole product. The other alkoxide copper complex, $Cu(OCH(CF_3)_2)(PPh_3)$ or $Cu(OCH(CF_3)_2)(PPh_3)_2$, which seems to exist in the reaction mixture of the reaction without PPh_3 addition, is not isolated from the products probably due to the lower crystallinity than that of **2a**. Table 1 summarizes the ^1H NMR data. The ^1H NMR spectrum of **2a** shows the signal due to the OCH hydrogen at 4.34 ppm accompanied by splitting due to H–F coupling. The peak area ratio between the phenyl hydrogens and the alkoxide hydrogen agrees well with the calculated value.

Fig. 1 shows molecular structure of **2a** determined by X-ray crystallography. Selected bond distances and angles are summarized in Table 2. The Cu center is in pseudotetrahedral coordination with the Cu–O distance of 2.087(6) Å and the Cu–P distances in the range 2.298–2.392 Å. The Cu–O bond distances are longer than those of mononuclear Cu^{II} fluoroalkoxide, $Ba\{Cu[OCMe(CF_3)_2]_3\}_2$ (1.78–1.89 Å) [11]. Three P–Cu–P angles are almost equal to each other, while the O–Cu–P angles vary in the range 102.3–114.4° probably due to difference of steric interaction of a PPh_3 ligand with the fluoro alkoxide ligand among the three PPh_3 ligands. $CuCl(PPh_3)_3$ having a similar tetrahedral mononuclear coordination show similar three P–Cu–Cl angles to each other [12]. The C–O bond distance (1.35 Å) is somewhat shorter than the C–O single bonds in organic compounds similarly to the already reported

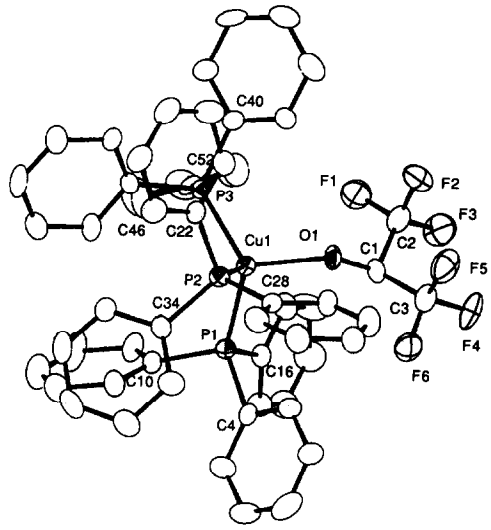


Fig. 1. Molecular structure of complex **2a** determined by X-ray crystallography.

TABLE 2. Selected bond distances (Å) and angles (°) of complexes **2a** and **4b**

	2a	**4b**	
Cu1–O1, (–O2)	2.087(6)	2.13(2)	2.12(2)
Cu2–O3, (–O4)	–	2.32(2)	2.03(2)
Cu1–P1	2.355(3)	2.335(5)	
Cu1–P2	2.392(2)	2.323(5)	
Cu1–P3	2.298(2)		
Cu2–P3	–	2.311(5)	
Cu2–P4	–	2.333(5)	
O1–C1, (O2–C2)	1.35(1)	1.41(6)	1.36(4)
O3–C45, (O4–C49)	–	1.26(4)	1.36(6)
Cu···Cu*	–	3.242(4)	3.243(4)
P1–Cu1–O1, (–O2)	108.3(2)	112.4(4)	112.3(4)
P2–Cu1–O1, (–O2)	102.3(2)	116.1(4)	114.5(4)
P3–Cu1–O1	114.4(2)	–	–
P3–Cu2–O3, (–O4)	–	114.3(4)	116.4(3)
P4–Cu2–O3, (–O4)	–	110.5(4)	114.0(4)
P1–Cu1–P2	110.66(9)	116.0(2)	–
P1–Cu1–P3	111.09(9)	–	–
P2–Cu1–P3	109.8(1)	–	–
P3–Cu2–P4	–	116.0(2)	–
Cu1–O1–C1, (–O2–C5)	133.8(5)	130.4(8)	130.2(6)
Cu2–O3–C45, (–O4–C49)	–	133.2(6)	127.1(6)
Cu1–O1–Cu1*, (–O2–)	–	99 (1)	99 (1)
Cu2–O3–Cu2*, (–O4–)	–	93 (1)	105 (1)
O1–Cu1–O2		80.6(5)	
O3–Cu2–O4		80.4(6)	

late transition metal alkoxides. The Cu–O–C bond angle (133.8°) is less acute than the M–O–C bond of the already reported Pt^{II} fluoro alkoxide with square-planar coordination [8d]. The M–O–C bond angles of late transition metal alkoxides are influenced by degree of repulsive interaction between the filled $d\pi$ orbital of the metal center and p-orbital of the coordinated oxygen [13]. Complex **2a** with a tetrahedral coordination seems to have the repulsive interaction to a smaller extent than the above fluoro alkoxide of d^8 metal center.

Reaction of **1** and diphenylmethanol below −5°C gives $Cu(OCHPh_2)(PPh_3)_3$ (**3a**), while the reaction with or without added PPh_3 at room temperature causes exclusive formation of $Cu(OCHPh_2)(PPh_3)_2$ (**3b**).

$$(Ph_3P)_2Cu\text{—}Me + HOCHPh_2 + PPh_3 \xrightarrow[(<-5\ ^\circ C)]{-CH_4} (Ph_3P)_3Cu\text{—}OCHPh_2 \quad \mathbf{3a}$$

$$(Ph_3P)_2Cu\text{—}Me + HOCHPh_2\ (+ PPh_3) \xrightarrow[r.t.]{-CH_4} (Ph_3P)_2Cu\text{—}OCHPh_2 \quad \mathbf{3b}$$

The ^1H NMR spectra of **3a** and **3b** show singlet peaks due to the OCH hydrogen at 5.84 ppm. The relative peak area ratios of the hydrogen to the phenyl hydrogens agree well with the proposed formula for **3a** and **3b**, respectively. The ^{13}C NMR spectrum of **3a** shows the signal due to the OCH carbon at 76.5 ppm with J(CH) value of 144 Hz. Although no difference in peak

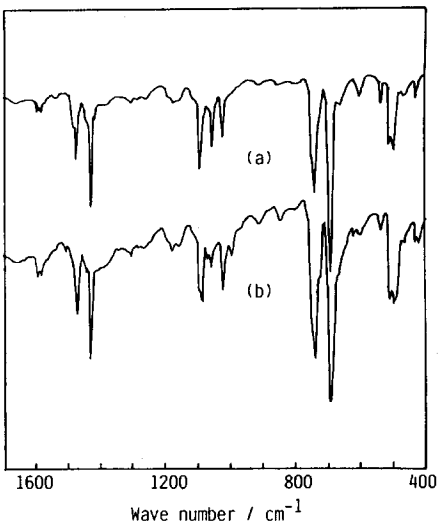


Fig. 2. IR spectra of (a) **3a** and (b) **3b** recorded in KBr disks.

positions of the NMR spectra is observed between **3a** and **3b**, these complexes show different IR spectra from each other as shown in Fig. 2. The difference in the IR spectra seems to include difference in the peak positions of ν(C–O) vibration which should appear in the region 1100–1300 cm^{-1}.

Reaction of phenol with **1** was reported to give $Cu(OPh)(PPh_3)_2$ (**4b**) exclusively [6a]. We have re-ex-

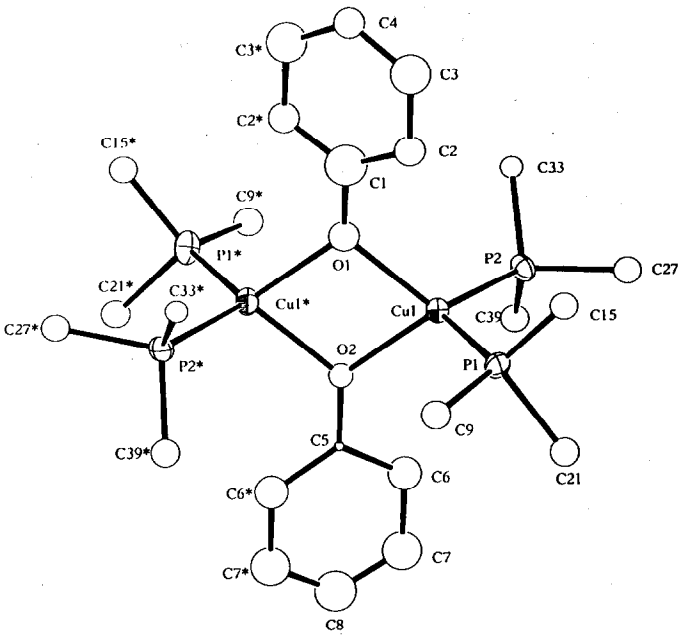


Fig. 3. Molecular structure of complex **4b** determined by X-ray crystallography. One of the two crystallographically independent molecules in a unit cell is shown. *o*-, *m*-, and *p*-phenyl carbons of the PPh_3 ligands are omitted for simplicity. The shown molecule contains a crystallographic C_2 axis along the line including C4, C1, O1, O2, C5, and C8 atoms. The atoms having number with asterisk is crystallographically equivalent to those having the same number without asterisk.

amined the reaction under various conditions and observed that reaction with PPh_3 addition gives $Cu(OPh)(PPh_3)_3$ (**4a**) in a high yield.

$$(Ph_3P)_2Cu{-}Me + HOPh + PPh_3 \xrightarrow{-CH_4} (Ph_3P)_3Cu{-}OPh \quad \textbf{4a}$$

Complex **4a** is prepared also from metathesis reaction of $CuCl(PPh_3)_3$ and NaOPh in a lower yield. Complexes **4a** and **4b** give satisfactory analytical results for the proposed formula. The ^1H NMR spectra of the complexes show peaks due to the PPh_3 hydrogens at 7.1–7.5 ppm and the phenoxide hydrogens at 6.3–6.8 ppm. Although the peak positions of the complexes are quite similar to each other the peak area ratios between the PPh_3 and the OPh ligands agree with the proposed formula in both complexes.

Fig. 3 shows crystal structure of **4b** containing two pseudotetrahedral Cu centers each of which is surrounded by two PPh_3 and by two bridging phenoxide ligands. Both of two crystallographically independent molecules in the unit cell have a crystallographic C_2 axis along the line including two oxygen and four carbon atoms of the phenoxide ligands (C4, C1, O1, O2, C5, and C8 atoms in the molecule shown in Fig. 3). Non-bonding distances between two copper centers in the molecules are 3.242 and 3.243 Å, which are longer than the corresponding distances of already reported halogen bridged dicopper(I) complexes (2.74–3.14 Å) [14]. Selected bond distances and angles are shown in Table 2. Comparison of the bond parameters in the phenoxide ligands with those of already reported transition metal phenoxide complexes seems to be infeasible because positional parameters of six atoms in the two phenoxide ligands in the molecule have low reliability due to the presence of the symmetry element.

2.2. *Reactions of alkoxide copper complexes with alcohols*

Complex **3a** reacts with $HOCH(CF_3)_2$ to give **2a** in a 66% yield, while reaction of **2a** with diphenylmethanol does not cause exchange of the alkoxide ligand.

$$(Ph_3P)_3Cu{-}OCHPh_2 \; (\textbf{3a}) + HOCH(CF_3)_2 \xrightarrow{-HOCHPh_2} (Ph_3P)_3Cu{-}OCH(CF_3)_2 \quad \textbf{2a}$$

Reaction of **3b** and $HOCH(CF_3)_2$ with addition of PPh_3 also gives **2a** in a 83% yield, while the reaction without PPh_3 addition gives a fluoro alkoxide complex $Cu(OCH(CF_3)_2)(PPh_3)_2$ (**2b**) in a 61% yield.

$$(Ph_3P)_2Cu{-}OCHPh_2 \; (\textbf{3b}) + HOCH(CF_3)_2 \xrightarrow[-HOCHPh_2]{+PPh_3} (Ph_3P)_3Cu{-}OCH(CF_3)_2 \quad \textbf{2a}$$

$$(Ph_3P)_2Cu{-}OCHPh_2 \; (\textbf{3b}) + HOCH(CF_3)_2 \xrightarrow{-HOCHPh_2} (Ph_3P)_2Cu{-}OCH(CF_3)_2 \quad \textbf{2b}$$

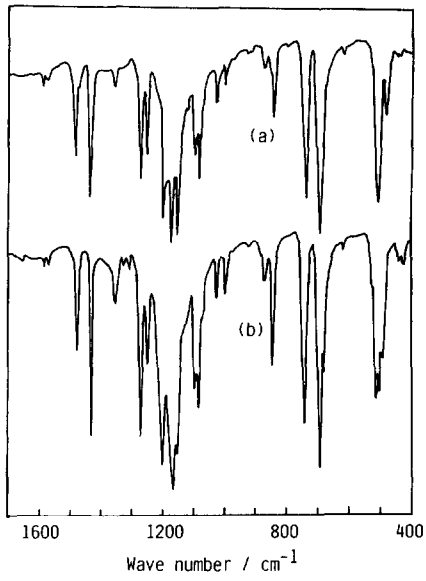


Fig. 4. IR spectra of (a) **2a** and (b) **2b** recorded in KBr disks.

Complex **2b** gives satisfactory elemental analyses and peak area ratio in the ^1H NMR spectrum. Although the ^1H NMR spectra of **2a** and **2b** show quite similar peak position of the OCH hydrogen to each other, they show difference from each other in peak positions of the phenyl hydrogens of the NMR spectra and in the IR peaks in the regions of 1200–1100 cm^{-1} and 550–450 cm^{-1} as shown in Fig. 4. Formation of **2a** or **2b** in the above reactions depending on the conditions is in contrast with the results of the reaction of **1** and the alcohol giving **2a** both in the presence or absence of the added PPh_3 ligands. Although complex **2b** is obtained from the above reaction mixture in good reproducibility of the yield, further standing the reaction mixture for several days causes separation of a small amount of crystals of **2a**. The result indicate gradual structural change from **2b** to **2a** in the solution and more facile crystallization of **2a** than **2b**.

Reactions of alkoxide copper complexes **2a** and **3a** with phenol cause the alkoxide ligand exchange to give complex **4b**.

$$(Ph_3P)_3Cu{-}OR \; (\textbf{2a}\ R = CH(CF_3)_2,\ \textbf{3a}\ R = CHPh_2) + HOPh \xrightarrow{-HOR} (Ph_3P)_2Cu{-}OPh \quad \textbf{4b}$$

Complex **4b** does not undergo any reaction on addition of $HOCH(CF_3)_2$ and $HOCHPh_2$.

Fig. 5 shows the ^1H NMR spectra of an equimolar mixture of **2a** and $HOCH(CF_3)_2$ both at −40°C and at 25°C. The spectra show OH hydrogen signals at −10.9 ppm at −40°C and at −9.3 ppm at 25°C, while free

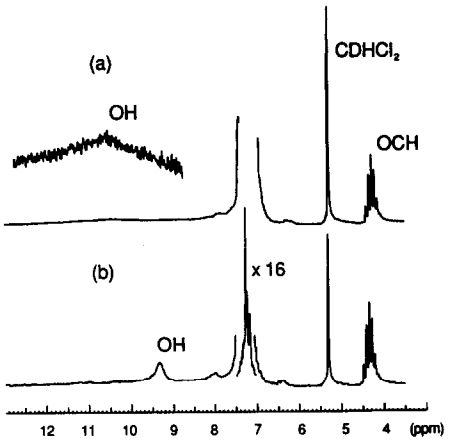


Fig. 5. The ^1H NMR spectra of an equimolar mixture of **2a** (28 mM) and $HOCH(CF_3)_2$ (28 mM) in CD_2Cl_2 at (a) −40°C and (b) 25°C.

$HOCH(CF_3)_2$ shows the OH hydrogen peak at 3.2 ppm at 25°C. The remarkably large shift of the peak position of the alcohol caused by the presence of **2a** is attributed to formation of $(PPh_3)_3Cu(OCH(CF_3)_2)$-$(HOCH(CF_3)_2)$ which has an O–H · · · O hydrogen bonding between the alkoxide ligand and alcohol. Solutions of mixtures of fluoro alcohol or phenol and fluoro alkoxide or phenoxide complexes of transition metals such as Pd, Pt, Rh, Ru, Re and Au have been reported to contain the alkoxide complexes with associated alcohol through strong O–H · · · O hydrogen bonding between the coordinated oxygen and OH group. The ^1H NMR spectra of the mixtures show the OH hydrogen peak at low magnetic field positions (9–14 ppm) [8,9,15–19]. Since the OH hydrogen peak in the spectrum of the mixture of **2a** and $HOCH(CF_3)_2$ is broadened, determination of the equilibrium constants by change of the peak positions depending on concentrations of the alcohol is not feasible. The OCH hydrogen peak appears as a single septet. The positions of the alkoxide CH hydrogen and of the CH hydrogen in the associated alcohol seem to be quite similar to each other because the peak position of the above mixture is quite similar to the peak in the ^1H NMR spectra of **2a** and to that of $HOCH(CF_3)_2$. Attempts to isolate the alkoxide complex with hydrogen bonded alcohol was not successful probably due to higher crystallinity of **2a** than the hydrogen bonded complex.

^1H NMR spectra of an equimolar mixture of $HOCHPh_2$ and **3a** show the OH hydrogen signal at 2.3 ppm which is quite similar to that of $HOCHPh_2$. The amount of the alkoxide complex with hydrogen bonded alcohol $(Ph_3P)_3Cu(OCHPh_2)(HOCHPh_2)$ in the mixture seems to be much smaller than the alkoxide complexes without associated alcohol.

2.3. Reactions of alkoxide copper complexes with 1,4-diethynylbenzene

Alkynyl copper complexes are regarded as important intermediates in coupling of alkynes [4,20] although number of the fully characterized compounds are small [21,22]. There have been no reports on multinuclear copper complexes with bridging dialkynyl ligands although the complexes in which copper centers are bridged by π-conjugated dialkynyl ligands would have a potential utility as the electrically conducting material [23]. On the other hand, alkoxides of Ru and Pt have been known as convenient precursor of the alkynyl complexes which are easily obtained from the reaction of the alkoxide complexes with terminal alkynes [24,25]. From these regards we have examined reaction of 1,4-diethynylbenzene with the alkoxide copper complex with expectation of formation of dinuclear copper(I) complexes with bridging dialkynyl ligands.

Complex **3a** reacts with 1,4-diethynylbenzene to give the copper complex formulated as $(Ph_3P)Cu(C{\equiv}CC_6H_4C{\equiv}C)Cu(PPh_3)$ (**5**). Complex **5** reacts with PEt_3 to give analogous PEt_3 coordinated complex $(Et_3P)Cu(C{\equiv}CC_6H_4C{\equiv}C)Cu(PEt_3)$ (**6**). The IR spectra of **5** and **6** show $\nu(C{\equiv}C)$ vibration peaks at 2042 cm^{-1} and 2040 cm^{-1}, respectively. No absorption due to the alkoxide ligand is observed. The IR results as well as elemental analyses indicate the above formula of the products. More detailed structure determination by NMR measurement or crystallography is not feasible due to extremely low solubility of the complexes to organic solvents. The low solubility may be due to the polymeric structure of the complexes with μ^2- or μ^3-coordinated bridging dialkynyl ligands.

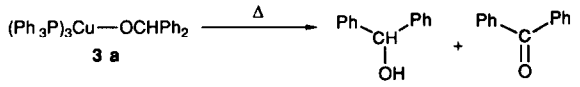
2.4. Other reactions

Complex **2a** reacts with phenyl acetate to give complex **4b**.

$$\underset{\textbf{2a}}{(Ph_3P)_3Cu{-}OCH(CF_3)_2} + MeCOOPh \longrightarrow \underset{\textbf{4b}}{(Ph_3P)_2Cu{-}OPh} + MeCOOCH(CF_3)_2$$

Similar exchange of the alkoxide group between the copper complex and carboxylic ester was already reported in the reaction of $(Ph_3P)_nCu(OR)$ (R = Me, Et, *etc.*) and esters [5], and the result was developed to catalytic *trans*-esterification which is of value as preparation or alcoholysis of esters under almost neutral conditions. Complex **2a** with lower nucleophilicity than the methoxide or ethoxide complexes due to electron withdrawing CF_3 groups in the alkoxide ligand also show high reactivity toward the above *trans*-esterification involving nucleophilic attack of the alkoxide ligand to the carbonyl carbon atom.

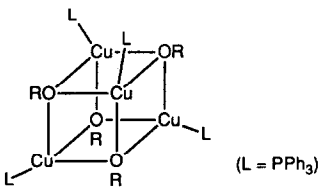
Thermolysis of complex **3a** gives a mixture of benzophenone and diphenylmethanol in almost 1:1 ratio.



The reaction is considered to involve initial β-hydrogen elimination of the alkoxide ligand followed by coupling of the alkoxide ligand with the resulting hydride ligand.

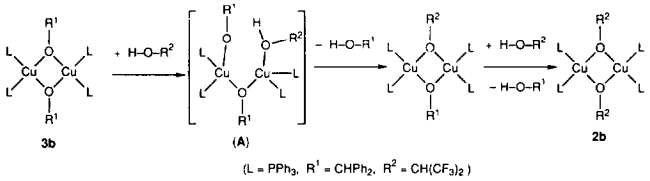
3. Discussion

Alkoxide copper complexes **2a**, **2b**, **3a**, and **3b** and phenoxide complex **4a** and **4b** contain the Cu centers ligated by two or three PPh_3 ligands. Tetrahedral coordination of the Cu^I center of **2a** is determined unambiguously by X-ray crystallography. Complexes **3a** and **4a** are assigned to monomeric structure with a tetrahedral Cu^I center similarly to **2a**. Complex **4b** having two PPh_3 ligands for one Cu center has dinuclear structure with two bridging phenoxide ligands based on the crystallographic results. It is natural to assign the dinuclear structures with bridging alkoxide ligands for **2b** and **3b** rather than another possible tricoordinated mononuclear structure that is much rarer than the dinuclear one. Previously reported PPh_3 coordinated copper complexes with alkoxide ligands such as OMe, OEt, and OPr groups have compositions of $Cu(OR)(PPh_3)$ or $Cu(OR)(PPh_3)_2$ [6], while the fluoro alkoxide, diphenylmethoxide, and phenoxide complexes in the present study have the composition of $Cu(OR)(PPh_3)_2$ or $Cu(OR)(PPh_3)_3$. The complexes with one or two PPh_3 ligands for a Cu center are believed to have di- or multinuclear structures with bridging alkoxide ligands. One of the probable structures for the composition, $Cu(OR)(PPh_3)$, is tetranuclear one which contains cubane type cluster core composed of four copper centers and of four μ^3-coordinated bridging alkoxide ligands as show below.



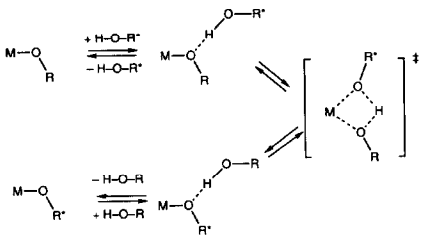
No formation of the mononuclear alkoxide complexes, $Cu(OR)(PPh_3)_3$, in the previous study agrees with the observation that the methoxide and ethoxide groups have higher basicity and smaller steric hindrance than the fluoro alkoxide or diphenylmethoxide groups and tend to coordinate to the metal centers as bridging ligands rather than non-bridging ligands.

Reaction of $HOCH(CF_3)_2$ with **3b** gives a dinuclear complex **2b** exclusively. It is in contrast with the formation of **2a** in the reaction mixture of **1** and $HOCH(CF_3)_2$ with and without addition of PPh_3. Scheme 1 shows probable reaction pathways for exchange of the alkoxide ligands and a possible interpretation for the dichotomy. Reaction of $HOCH(CF_3)_2$ with **3b** having the dinuclear structure with bridging alkoxide ligands proceeds through dinuclear intermediate to give **2b**, while the reaction with **3a** proceeds through mononuclear intermediates to lead formation of **2a** as the major product. Reaction of $HOCH(CF_3)_2$ with **1** seems to give a mixture of several alkoxide copper complexes including **2a** and **2b**. Preferential isolation of **2a** from the reaction mixture is probably due to higher crystallinity of **2a**. Standing the solution of **2b** causes gradual separation of **2a** as crystals in a small amount, indicating higher crystallinity of **2a**, formed by reaction of **2b** with PPh_3 partially dissociated from the complexes in the mixture, than **2b**. Products of the reaction of $HOCH(CF_3)_2$ with **1** seem to contain the copper alkoxide with other composition such as $Cu(OCH(CF_3)_2)(PPh_3)$ or $Cu(OCH(CF_3)_2)$, while these complexes are not isolated as the crystals from the mixtures.

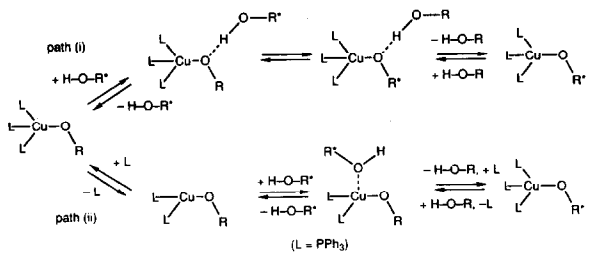


Scheme 1. Postulated reaction pathway for alkoxide ligand exchange of **3b**. (A) denotes a possible intermediate with dinuclear structure.

Reactions of **2a** with phenol and with phenyl acetate give **4b** in a high yield although mononuclear phenoxide **4a** is obtained independently from the reaction of phenol and **1** with PPh_3 addition. Preferential formation of **4b** in the former reactions is due to higher stability of the complex with phenoxide bridged structure than **4a** or due to higher crystallinity of **4b** than **4a**. Relative stability of the complex **4b** to **4a** in solu-



Scheme 2. Pathway for alkoxide exchange proposed for Pd, Pt, and Ru complexes.



Scheme 3. Possible reaction pathways for ligand exchange of the alkoxide copper complexes.

tion is not determined because they show ^1H NMR peaks at quite similar positions to each other.

Exchange of the alkoxide ligand of Pd^{II} and Pt^{II} complexes is believed to proceed through initial formation of intermediate alkoxide complex with associated alcohol through O–H···O hydrogen bonding. The corresponding fluoro alkoxide and phenoxide complexes with hydrogen bonded alcohols were isolated. Calorimetric studies and detailed NMR measurement of the above mixtures show the plausibility of the above ligand exchange mechanism (Scheme 2). The ^1H NMR spectra of an equimolar mixture of **2a** and $HOCH(CF_3)_2$ shows the OH hydrogen peak at low magnetic field position, indicating the presence of the alkoxide complexes with hydrogen bonded alcohol in a large amount. This result seems to agree with the pathway involving the intermediate alkoxide complexes with hydrogen bonded alcohols for the ligand exchange reaction (path (i) in Scheme 3). On the other hand, PPh_3 group coordinated to the Cu^I center, which is labile due to the d^{10} configuration, tends to undergo facile dissociation in the solutions. The other pathway involving initial PPh_3 dissociation (path (ii) in Scheme 3) is also possible for the alkoxide ligand exchange. At present we do not have sufficient experimental results to compare the probability among the above two reaction pathways for alkoxide ligand substitution by alcohol.

4. Experimental details

All the manipulations of the complexes were carried out under nitrogen or argon using Schlenk technique. Solvents were dried in usual manners, distilled and stored under nitrogen atmosphere. $CuMe(PPh_3)_2$-$(Et_2O)_{0.5}$ (**1**), $Cu(OPh)(PPh_3)_2$ (**4b**), and 1,4-diethynylbenzene were prepared according to the literature [7,26,27]. IR spectra were measured on a JASCO 810 spectrophotometer. NMR spectra (^1H, ^{13}C, and ^{31}P) were recorded on JEOL FX-100, GX-270, and GX-500 spectrometers. Elemental analyses were carried out by Yanagimoto Type MT-2 CHN autocorder. GC analysis was carried out by using Shimadzu GC-8A.

4.1. Preparation of $Cu(OCH(CF_3)_2)(PPh_3)_3$ (2a)

To an Et_2O (4 ml) solution of **1** (1.33 g, 2.1 mmol) and PPh_3 (540 mg, 2.1 mmol) was added $(CF_3)_2CHOH$ (370 mg, 2.4 mmol) at −5°C. Stirring the reaction mixture for 2 h caused gradual separation of a white solid from the reaction mixture. The white solid product was filtered, washed with Et_2O several times and dried in vacuo. Recrystallization from a minimum amount of toluene gave **2a** as colorless crystals (1.46 g, 68%). Anal. Found: C, 66.8; H, 4.6. Calcd. for $C_{57}H_{46}$-CuF_6OP_3: C, 67.3; H, 4.6.

Similar reaction without added PPh_3 gave **2a** in 30% yield. No other solid products were isolated.

4.2. Preparation of $Cu(OCHPh_2)(PPh_3)_3$ (3a) and $Cu(OCHPh_2)(PPh_3)_2$ (3b)

To a mixture of **1** (1.73 g, 2.7 mmol), PPh_3 (780 mg, 3.0 mmol), and Ph_2CHOH (600 mg, 3.3 mmol) was added THF (20 ml) at −15°C with stirring. The complex was dissolved gradually on stirring at the temperature to give a brown yellow solution from which a white solid began to precipitate. After the reaction for 7 h the formed solid was filtered and washed with Et_2O to give **3a** (2.1 g, 75%). Anal. Found: C, 77.7; H, 5.6. Calcd. for $C_{67}H_{56}CuOP_3$: C, 77.9; H, 5.5.

Similar reaction without addition of PPh_3 gave $Cu(OCHPh_2)(PPh_3)_2$ (**3b**) (86%). Anal. Found: C, 75.6; H, 5.6. Calcd. for $C_{49}H_{41}CuOP_2$: C, 76.3; H, 5.4.

4.3. Preparation of $Cu(OPh)(PPh_3)_3$ (4a)

4.3.1. Method (i)

To a mixture of **1** (310 mg, 0.48 mmol), PPh_3 (140 mg, 0.53 mmol), and PhOH (54 mg, 0.58 mmol) was added Et_2O (3 ml) at −10°C. Stirring the colorless solution at the temperature caused deposition of a pale yellow solid the color of which was gradually turned into off white. After the reaction for 7 h the solid product was filtered, washed with Et_2O and recrystallized from toluene to give **4a** (340 mg, 75%). Anal. Found: C, 76.2; H, 5.6. Calcd. for $C_{60}H_{50}CuOP_3$: C, 76.4; H, 5.3.

4.3.2. Method (ii)

To a mixture of $CuCl(PPh_3)_3$ (800 mg, 0.90 mmol) and NaOPh (90 mg, 1.1 mmol) was added toluene (15 ml) at room temperature. Stirring the mixture caused gradual dissolution of the materials to give a colorless solution from which a white solid began to precipitate. After the reaction for 5 h the mixture was filtered by passing a Celite column. The filtrate was condensed to

TABLE 3. Crystallographic data and details of structure refinement of complexes **2a** and **4b**

Complex	**2a**	**4b**
Chemical formula	$C_{57}H_{46}CuF_6OP_3$	$C_{84}H_{70}Cu_2O_2P_4$
Formula weight	1017.08	1362.46
Crystal system	orthorhombic	monoclinic
Space group	$Pn2_1a$ (No. 33)	$P2$ (No. 3)
a, Å	18.804(2)	13.955(3)
b, Å	19.655(4)	17.610(3)
c, Å	13.175(3)	13.961(3)
β, °	–	90.06(2)
V, Å^3	4869	3430
Z	4	2
μ, cm^{-1}	6.07	7.62
$F(000)$	2096	1416
ρ_{calcd}, g cm^{-3}	1.388	1.319
Crystal size, mm×mm×mm	0.3×0.3×0.4	0.3×0.4×0.4
2θ range, deg	3.0–55.0	5.0–50.0
Scan rate, deg min^{-1}	4	8
Unique reflections	4416	6530
Used reflections ($F_o \geq 3\sigma(F_o)$)	2800	4162
$R(F_o)$ [a]	0.053	0.103
$Rw(F_o)$ [a]	0.051	0.101
Weighting scheme	$[\{\sigma(F_o)\}^2 + \{0.020(F_o)\}^2]^{-1}$	$[\{\sigma(F_o)\}^2]^{-1}$

[a] $R = \Sigma\|\|F_o| - |F_c\|/\Sigma|F_o|$, $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

give **4a** as a white solid which was filtered, washed with Et_2O, and dried in vacuo (360 mg, 43%). Anal. Found: C, 76.0; H, 5.8.

4.4. *Crystal structures determination of 2a and 4b*

Crystallographic data and details of structure refinement are summarized in Table 3.

Crystal of **2a** suitable for crystallography was obtained from CD_2Cl_2 containing $HOCH(CF_3)_2$ and mounted in a glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with $19 \leq 2\theta \leq 22°$. Intensities were collected on Rigaku AFC-5 automated four-cycle diffractometers by using Mo-Kα radiation ($\lambda = 0.710\ 69$ Å) and the ω–2θ method. Calculations were carried out by using a program package SAPI85 on a FACOM A-70 computer. A full matrix least-squares refinement was carried out by applying anisotropic thermal factors to all the non-hydrogen atoms. Hydrogen atoms were located from calculation by assuming the ideal positions (d(C–H) = 0.95 Å) and included the structure calculation without further refinement of the parameters. Absorption correction by Gaussian integration of the collected data was applied. Crystallographic data and atomic coordinates of the non-hydrogen atoms are listed in Tables 3 and 4, respectively.

Crystal of **4b** suitable for crystallography was obtained from a toluene-hexane mixture and mounted in a glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with $19 \leq 2\theta \leq 22°$. Intensities were collected on Rigaku AFC-5R automated four-cycle diffractometers by using Mo-Kα radiation ($\lambda = 0.710\ 69$ Å) and the ω–2θ method. Calculations were carried out by using a program package TEXSAN on a DEC Micro VAXII computer. The unit cell contains two molecules each of which has a crystallographic C_2 axis along the line including two phenoxide oxygen atoms. Positional and thermal parameters of C5 carbons atom on the symmetry unit are not well converged due to the low occupancy. The insufficient convergence in the structure calculations prevented from application of anisotropic thermal factors to the atoms other than Cu and P atoms. Atomic coordinates of the non-hydrogen atoms are listed in Table 5.

Additional material available from the authors comprises H-atom coordinates, thermal parameters and all the bond distances and angles.

4.5. *Reaction of $HOCH(CF_3)_2$ with 3a*

To an Et_2O (2 ml) suspension of **3a** (230 mg, 0.22 mmol) was added $HOCH(CF_3)_2$ (53 mg, 0.34 mmol) at room temperature. After stirring the mixture for 7 h the resulting white solid was filtered and dried in vacuo to give **2a** as a white solid (150 mg, 67%). The IR and ^{1}H NMR spectra as well as elemental analysis agreed with that of **2a**.

4.6. *Reaction of $HOCH(CF_3)_2$ with 3b*

To an Et_2O (6 ml) suspension of **3b** (470 mg, 0.61 mmol) was added $HOCH(CF_3)_2$ (140 mg, 0.91 mmol) at room temperature with stirring. The starting materials were gradually dissolved to give a colorless solution. After the reaction for 7 h the solution was cooled to −70°C to afford **2b** as a white solid which was filtered, washed with Et_2O and dried *in vacuo* (380 mg, 61%). Anal. Found: C, 61.8; H, 4.2. Calcd. for $C_{39}H_{31}CuF_6OP_2$: C, 62.0; H, 4.1.

Similar reaction of **3b** with $HOCH(CF_3)_2$ with addition of PPh_3 gave **2a** (83%).

4.7. *Reaction of phenol with 2a*

To a mixture of **2a** (370 mg, 0.36 mmol) and phenol (51 mg, 0.54 mmol) was added Et_2O (3 ml) at room temperature with stirring. After the reaction for 7 h the resulting white solid was filtered, washed with Et_2O, and dried *in vacuo* to give **4b** as a colorless solid (190 mg, 78%). The IR and ^{1}H NMR spectra as well as elemental analysis agreed with that of **4b**.

TABLE 4. Atomic coordinates and equivalent isotropic temperature factors of **2a**

Atom	x	y	z	B_{eq}
Cu	0.97985(5)	0.2500	0.21816(7)	3.07
P1	0.88181(13)	0.31235(13)	0.27896(19)	3.11
P2	0.97863(11)	0.24506(16)	0.03675(15)	3.03
P3	0.98050(13)	0.14164(10)	0.28358(18)	2.95
O1	1.0721(3)	0.3059(3)	0.2473(4)	3.7
F1	1.1095(4)	0.2583(4)	0.4379(5)	7.0
F2	1.2017(4)	0.2898(4)	0.3567(6)	7.7
F3	1.1596(4)	0.3523(4)	0.4772(6)	8.5
F4	1.1526(4)	0.4550(3)	0.3497(5)	7.0
F5	1.1855(4)	0.3971(4)	0.2235(6)	7.8
F6	1.0852(4)	0.4469(3)	0.2203(5)	6.8
C1	1.0920(5)	0.3487(5)	0.3222(8)	3.6
C2	1.1416(7)	0.3142(6)	0.3962(8)	5.1
C3	1.1299(6)	0.4119(5)	0.2797(9)	4.6
C4	0.8679(6)	0.3926(5)	0.2088(8)	3.5
C5	0.9257(6)	0.4191(5)	0.1631(7)	4.0
C6	0.9222(7)	0.4788(6)	0.1087(10)	5.1
C7	0.8576(9)	0.5118(6)	0.0982(10)	6.4
C8	0.7989(7)	0.4858(7)	0.1452(11)	6.2
C9	0.8015(6)	0.4244(6)	0.2001(8)	4.7
C10	0.7949(4)	0.2703(4)	0.2792(8)	3.6
C11	0.7695(5)	0.2400(6)	0.3674(8)	4.7
C12	0.7069(7)	0.2013(7)	0.3623(10)	6.9
C13	0.6703(7)	0.1963(7)	0.2752(12)	6.9
C14	0.6938(6)	0.2271(7)	0.1891(10)	6.2
C15	0.7567(5)	0.2646(6)	0.1895(7)	4.6
C16	0.8887(5)	0.3420(5)	0.4115(7)	3.2
C17	0.9413(6)	0.3118(6)	0.4711(8)	4.9
C18	0.9464(8)	0.3274(7)	0.5707(10)	7.5
C19	0.9000(8)	0.3738(8)	0.6161(9)	6.5
C20	0.8470(7)	0.4013(7)	0.5591(9)	5.3
C21	0.8407(6)	0.3858(6)	0.4559(8)	4.7
C22	1.0152(5)	0.1680(4)	−0.0202(7)	2.9
C23	0.9904(6)	0.1374(6)	−0.1094(7)	4.6
C24	1.0235(7)	0.0785(5)	−0.1471(8)	5.1
C25	1.0814(7)	0.0519(6)	−0.1010(9)	5.6
C26	1.1086(7)	0.0818(7)	−0.017(11)	6.0
C27	1.0751(6)	0.1409(6)	0.0251(8)	4.2
C28	1.0275(5)	0.3110(5)	−0.0369(7)	3.1
C29	1.0761(6)	0.3510(6)	0.0129(8)	4.0
C30	1.1140(7)	0.4002(6)	−0.0374(10)	5.6
C31	1.1035(6)	0.4085(6)	−0.1420(10)	5.6
C32	1.0563(6)	0.3678(7)	−0.1917(8)	5.5
C33	1.0181(6)	0.3182(6)	−0.1390(7)	4.6
C34	0.8887(4)	0.2513(6)	−0.0169(6)	3.5
C35	0.8612(6)	0.3125(7)	−0.0456(9)	4.7
C36	0.7899(7)	0.3187(7)	−0.0804(10)	6.1
C37	0.7504(5)	0.2601(8)	−0.0900(9)	6.0
C38	0.7788(7)	0.1995(7)	−0.0613(11)	6.0
C39	0.8463(6)	0.1935(5)	−0.0243(8)	3.8
C40	1.0670(5)	0.1005(5)	0.2941(7)	3.5
C41	1.0725(6)	0.0312(5)	0.3211(8)	4.4
C42	1.1396(7)	0.0010(5)	0.3256(9)	5.5
C43	1.2000(7)	0.0396(7)	0.3067(8)	5.7
C44	1.1938(6)	0.1081(7)	0.2830(10)	5.7
C45	1.1275(5)	0.1378(5)	0.2759(7)	3.7
C46	0.9257(5)	0.0856(5)	0.2066(7)	2.9
C47	0.9538(5)	0.0329(5)	0.1460(7)	3.6
C48	0.9076(6)	−0.0054(6)	0.0856(8)	4.5
C49	0.8361(7)	0.0063(6)	0.0859(8)	4.9
C50	0.8086(5)	0.0602(6)	0.1400(8)	4.6
C51	0.8532(6)	0.0995(6)	0.1990(8)	3.8
C52	0.9471(5)	0.1267(4)	0.4125(7)	3.5
C53	0.9920(6)	0.1443(7)	0.4943(8)	5.3
C54	0.9685(7)	0.1406(7)	0.5924(9)	6.2
C55	0.9017(8)	0.1165(8)	0.6153(10)	6.7
C56	0.8599(8)	0.0964(10)	0.5366(11)	8.1
C57	0.8800(6)	0.1044(7)	0.4385(8)	5.3

$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

4.8. Reaction of diphenylmethanol with 2a

To a mixture of **2a** (380 mg, 0.37 mmol) and diphenylmethanol (110 mg, 0.60 mmol) was added THF (4 ml) with stirring at room temperature. After the reaction for 24 h the solvent was removed from the colorless solution to dryness, and the resulting white solid was washed with Et_2O several times and dried *in vacuo* (270 mg, 72% as **2a**). The IR spectrum was identical with that of **2a**.

Reactions of **4b** with $HOCH(CF_3)_2$ and with diphenylmethanol were carried out analogously.

4.9. Reaction of phenyl acetate with 2a

To an Et_2O (4 ml) solution of **2a** (420 mg, 0.41 mmol) was added phenyl acetate (74 mg, 0.62 mmol) at room temperature with stirring. After the reaction for 7 h at room temperature the resulting white solid was filtered, washed with Et_2O and dried in vacuo to yield **4b** (270 mg, 97%). GC analyses of the filtrate shows formation of $MeCOOCH(CF_3)_2$ in 88%. The IR and ^1H NMR spectra as well as elemental analysis agreed with that of **4b**.

4.10. Thermolysis of 3a

Complex **3a** (53 mg, 0.051 mmol) was transferred to a Schlenk flask and heated by an oil bath. The complex began to melt around 100°C to give a white oily material which darkened on raising the temperature. After heating for 20 min at 200°C the organic products were extracted with Et_2O (2 ml) and analyzed by GC which revealed formation of benzophenone (45%) and diphenylmethanol (42%).

4.11. Preparation of $(R_3P)Cu(C{\equiv}CC_6H_4C{\equiv}C)Cu(PR_3)$ (5, R = Ph; 6, R = Et)

To a mixture of **3a** (240 mg, 0.23 mmol) and 1,4-diethylbenzene (15 mg, 0.12 mmol) was added Et_2O (2 ml) at room temperature with stirring. The reaction for 2 h caused precipitation of a yellow solid which was filtered off and washed with hexane to give **5** (86 mg,

TABLE 5. Atomic coordinates and equivalent isotropic temperature factors of **4b**

Atom	x	y	z	B_{eq} or B_{iso} [a]
Cu(1)	0.5863(2)	0.0089	0.4224(2)	2.73(5)
Cu(2)	0.0777(2)	0.5086(5)	0.0865(2)	2.79(6)
P(1)	0.5514(4)	0.0092(9)	0.2588(3)	3.1(1)
P(2)	0.7479(3)	0.0116(8)	0.4626(3)	2.8(1)
P(3)	0.0379(4)	0.5080(8)	0.2471(3)	2.8(1)
P(4)	0.2411(3)	0.5110(8)	0.0515(3)	3.0(1)
O(1)	0.5000	−0.070(2)	0.5000	3.8(9)
O(2)	0.5000	0.087(2)	0.5000	2.3(7)
O(3)	0.0000	0.595(2)	0.0000	3.2(7)
O(4)	0.0000	0.439(1)	0.0000	1.5(5)
C(1)	0.5000	−0.149(4)	0.5000	7(1)
C(2)	0.534(2)	−0.184(2)	0.418(2)	3.8(5)
C(3)	0.534(2)	−0.268(2)	0.421(2)	6.4(8)
C(4)	0.5000	−0.306(3)	0.5000	3(1)
C(5)	0.5000	0.164(2)	0.5000	0.3(6)
C(6)	0.582(2)	0.203(2)	0.474(2)	4.4(6)
C(7)	0.578(2)	0.288(2)	0.471(2)	6.0(8)
C(8)	0.5000	0.324(4)	0.5000	6(1)
C(9)	0.427(1)	0.022(2)	0.220(1)	3.4(5)
C(10)	0.399(2)	0.046(2)	0.151(2)	6.0(8)
C(11)	0.289(3)	0.44(2)	0.118(2)	7.6(10)
C(12)	0.240(3)	−0.016(2)	0.154(3)	8(1)
C(13)	0.278(2)	−0.062(2)	0.229(2)	7.2(9)
C(14)	0.365(2)	−0.059(2)	0.256(2)	6.1(7)
C(15)	0.599(2)	−0.068(2)	0.192(2)	3.0(8)
C(16)	0.693(3)	−0.097(2)	0.220(2)	7.8(9)
C(17)	0.749(4)	−0.151(4)	0.147(4)	16(1)
C(18)	0.680(3)	−0.191(2)	0.086(3)	5.9(10)
C(19)	0.615(3)	−0.165(3)	0.060(3)	11(1)
C(20)	0.556(2)	−0.099(2)	0.110(2)	6.1(8)
C(21)	0.603(2)	0.094(2)	0.191(3)	3.2(8)
C(22)	0.593(2)	0.157(2)	0.237(2)	5.3(7)
C(23)	0.635(2)	0.228(2)	0.196(2)	6.8(8)
C(24)	0.683(3)	0.224(3)	0.109(3)	8(1)
C(25)	0.665(3)	0.155(3)	0.061(3)	9(1)
C(26)	0.637(2)	0.088(2)	0.102(2)	4.6(6)
C(27)	0.830(1)	0.001(2)	0.363(1)	3.0(5)
C(28)	0.893(2)	0.059(2)	0.341(2)	6.1(8)
C(29)	0.961(2)	0.056(2)	0.250(2)	6.4(8)
C(30)	0.943(2)	−0.008(2)	0.197(2)	6.1(8)
C(31)	0.879(2)	−0.066(2)	0.216(2)	5.5(7)
C(32)	0.815(2)	−0.054(2)	0.305(2)	4.8(6)
C(33)	0.789(2)	−0.066(2)	0.543(2)	2.0(5)
C(34)	0.876(2)	−0.072(2)	0.573(2)	5.4(7)
C(35)	0.915(3)	−0.138(2)	0.622(3)	7(1)
C(36)	0.862(2)	−0.200(2)	0.628(2)	5.2(8)
C(37)	0.776(2)	−0.202(2)	0.570(2)	6.8(8)
C(38)	0.734(2)	−0.139(2)	0.521(2)	5.0(6)
C(39)	0.786(2)	0.097(2)	0.524(2)	3.1(7)
C(40)	0.875(2)	0.124(2)	0.517(2)	7.4(9)
C(41)	0.897(3)	0.182(2)	0.604(2)	5.9(9)
C(42)	0.835(3)	0.212(3)	0.652(3)	8(1)
C(43)	0.751(3)	0.167(2)	0.683(3)	9(1)
C(44)	0.720(2)	0.109(2)	0.608(2)	4.7(6)
C(45)	0.0000	0.667(2)	0.0000	0.5(6)
C(46)	0.031(2)	0.701(2)	0.078(2)	4.4(6)
C(47)	0.027(2)	0.787(2)	0.084(2)	6.1(8)
C(48)	0.0000	0.824(3)	0.0000	3(1)
C(49)	0.0000	0.362(4)	0.0000	5(1)
C(50)	0.076(2)	0.314(2)	0.034(2)	4.8(6)
C(51)	0.075(2)	0.233(2)	0.035(2)	6.2(8)
C(52)	0.0000	0.198(4)	0.0000	7(1)
C(53)	0.138(1)	0.503(2)	0.329(1)	3.2(5)
C(54)	0.156(2)	0.464(2)	0.398(2)	4.9(7)
C(55)	0.251(2)	0.463(2)	0.447(2)	6.7(9)
C(56)	0.300(2)	0.529(2)	0.448(2)	6.3(8)
C(57)	0.288(2)	0.587(2)	0.371(2)	5.4(7)
C(58)	0.195(2)	0.575(2)	0.319(2)	4.5(6)
C(59)	−0.040(3)	0.429(2)	0.288(3)	5(1)
C(60)	−0.076(2)	0.429(2)	0.380(2)	5.3(7)
C(61)	−0.128(2)	0.360(2)	0.413(2)	6.4(9)
C(62)	−0.119(2)	0.299(2)	0.361(2)	4.0(6)
C(63)	−0.073(2)	0.291(2)	0.271(2)	5.5(7)
C(64)	−0.020(2)	0.361(2)	0.235(2)	5.4(7)
C(65)	−0.031(2)	0.591(2)	0.291(2)	1.4(6)
C(66)	−0.027(3)	0.619(2)	0.375(2)	8.0(10)
C(67)	−0.099(2)	0.684(2)	0.400(2)	5.1(7)
C(68)	−0.159(2)	0.709(2)	0.338(2)	5.1(7)
C(69)	−0.190(3)	0.664(3)	0.249(3)	12(1)
C(70)	−0.113(2)	0.608(2)	0.221(2)	6.5(8)
C(71)	0.317(2)	0.432(2)	0.106(2)	3.7(8)
C(72)	0.396(2)	0.440(2)	0.144(2)	4.5(6)
C(73)	0.436(2)	0.367(2)	0.174(3)	8.0(10)
C(74)	0.403(2)	0.302(2)	0.165(2)	5.3(8)
C(75)	0.305(2)	0.293(2)	0.137(2)	5.4(7)
C(76)	0.264(2)	0.363(2)	0.091(2)	5.2(7)
C(77)	0.299(2)	0.594(2)	0.095(2)	2.1(6)
C(78)	0.277(3)	0.621(2)	0.187(3)	10(1)
C(79)	0.349(4)	0.671(4)	0.244(4)	17(2)
C(80)	0.405(4)	0.716(3)	0.197(4)	9(1)
C(81)	0.437(3)	0.682(3)	0.112(3)	10(1)
C(82)	0.391(2)	0.617(2)	0.060(2)	7.7(9)
C(83)	0.283(1)	0.516(2)	−0.073(1)	3.4(4)
C(84)	0.348(2)	0.551(2)	−0.106(2)	4.9(7)
C(85)	0.383(2)	0.545(2)	−0.214(2)	6.3(8)
C(86)	0.348(2)	0.518(4)	−0.271(2)	10.7(10)
C(87)	0.283(3)	0.443(3)	−0.224(3)	10(1)
C(88)	0.240(2)	0.448(2)	−0.132(2)	6.3(8)

[a] $B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$ is applied to Cu and P atoms. B_{iso} is shown for O and C atoms.

96%). Anal. Found: C, 70.3; H, 4.4. Calcd. for $C_{46}H_{34}Cu_2P_2$: C, 71.2; H, 4.4.

To an Et_2O (1 ml) dispersion of **5** (39 mg, 0.050 mmol) was added PEt_3 (120 mg, 1.0 mmol) at room temperature. The yellow reaction mixture was turned into pale yellow. After stirring for 12 h the resulting pale yellow solid was washed with Et_2O several times to give **6** (4 mg, 16%). Anal. Found: C, 54.6; H, 8.4. Calcd. for $C_{22}H_{34}Cu_2P_2$: C, 54.2; H, 7.0.

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