Preparation of Organic Copper(I) Complexes by the Reactions of Methylbis(triphenylphosphine)copper(I) with Nitroalkanes, β-Diketones, and Cyanoalkanes[1)]

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Reactions of a methylcopper complex $CH_3Cu(PPh_3)_2$(diethyl ether)$_{0.5}$ (PPh_3=triphenylphosphine) with three types of active hydrogen compounds HA give the corresponding copper derivatives of active hydrogen compounds formulated as $ACu(PPh_3)_2$. Nitroalkanes (nitromethane, nitroethane and 2-nitropropane) form copper complexes bonded through aci-nitro groups. β-Diketone and its analogs such as acetylacetone, diethyl malonate and ethyl acetoacetate react in their enol form to give six-membered *O,O′*-bonded chelates, whereas cyanoalkanes including acetonitrile, propionitrile, and malononitrile afford organocopper complexes having a direct Cu–C bond.

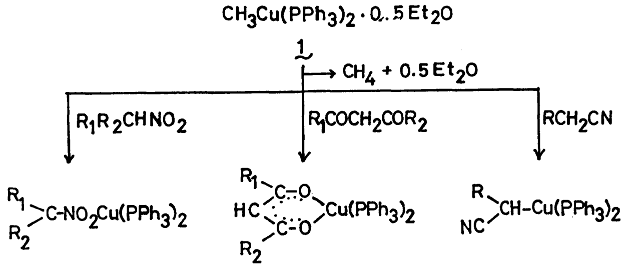
The non-transition metal derivatives of active hydrogen compounds such as diethyl malonate and malononitrile serve as convenient and versatile starting materials for the syntheses of various organic compounds. Extensive studies have been made on the preparation and properties of the non-transition metal derivatives of the active hydrogen compounds. However, only limited information is available on the transition metal derivatives of the active hydrogen compounds except for some β-diketones which form chelate complexes with the transition metals. In the course of studies on the chemical properties of alkylcopper complexes having tertiary phosphine ligands[2)] it was found that reactions proceed smoothly between the alkylcopper complexes and various active hydrogen compounds having nitro, β-dicarbonyl, or cyano group to afford various copper derivatives of the active hydrogen compounds in high yields.

In this paper we report the preparation of the copper derivatives of the active hydrogen compounds and discuss their structures. Marsich and Camus and co-workers recently reported the preparation of copper derivatives of active hydrogen compounds having β-dicarbonyl or nitro group by the reaction of arylcopper(I) with the active hydrogen compounds in the presence of phosphine ligands.[3)] Tsuda *et al.* reported the formation of (cyanomethyl)copper complexes by the decarbonylation of Cu(I) and Cu(II) cyanoacetates as well as by the reaction of $t\text{-}C_4H_9OCu(P(n\text{-}C_4H_9)_3)$ with CH_3CN.[4)] Utilization of (cyanomethyl)copper prepared *in situ* by the reaction of CuI with $LiCH_2CN$ for organic syntheses[5)] was also reported.

Results and Discussion

Reactions of Alkylcopper Complexes with Active Hydrogen Compounds. Alkylcopper complexes smoothly react with active hydrogen compounds having nitro, β-dicarbonyl, or cyano group. The methylcopper complex $CH_3Cu(PPh_3)_2(Et_2O)_{0.5}$ gives three types of complex in high yields (63—92%) depending on the nature of the active hydrogen compound.

An active hydrogen compound with more acidic hydrogen reacts more easily with the methylcopper complex. As an example, **1** reacts with malononitrile immediately at −30 °C, but the reaction of **1** with propionitrile at room temperature takes several hours to complete. All the complexes prepared are white indicating that the oxidation number of copper in the complexes is one. Type **2** and **3** complexes are soluble in organic solvents, but not the copper derivatives of cyanoalkanes, **4**. Most complexes are relatively insensitive to air, having very high thermal stability in the solid state. However, they are easily oxidized in solution, the thermal stability decreasing.



2 **3** **4**

2a $R_1=R_2=H$
2b $R_1=CH_3$, $R_2=H$
2c $R_1=R_2=CH_3$

3a $R_1=R_2=CH_3$
3b $R_1=R_2=OC_2H_5$
3c $R_1=CH_3$, $R_2=OC_2H_5$

4a R=H
4b $R=CH_3$
4c R=CN

Fig. 1.

Of the products represented in Fig. 1, **2a**, **3a**, **3b**, **3c**, and **5** have been independently prepared by Marsich and Camus and co-workers through reactions of arylcopper(I) prepared *in situ* with the corresponding active hydrogen compounds in the presence of PPh_3.[3)] However, no NMR spectroscopic data have been given.[6)] Analytical and spectral data of the isolated complexes are summarized in Tables 1 and 2, respectively.

In addition to the nitromethanato complex **2a** they prepared a dinitrophenylmethane derivative of copper $(C_6H_5C(NO_2)_2)Cu(PPh_3)_2$, and confirmed by X-ray analysis that the copper atom in the complex is bonded to the dinitrophenylmethanato ligand through one of the two nitro groups in the solid state.[3d)] The IR and NMR spectroscopic data of complexes **2a**, **2b**, and **2c** support the view that the copper atom in these complexes is bonded to the nitroalkanato ligand through the same type of bonding (aci-nitro type bonding) as in the dinitrophenylmethane complex:

The ν(C=N) stretching frequencies of the nitroalkanes

TABLE 1. PREPARATION OF THE COPPER DERIVATIVES OF ACTIVE HYDROGEN COMPOUNDS ACCORDING TO Fig. 1.

Complex		Yield (%)	Mp (°C)	Found (Calcd), % C	H	N	M_w[a]
$Cu(CH_2NO_2)(PPh_3)_2$	**2a**[b]	89	177—182	68.7 (68.5	5.1 5.0	2.4 2.2)	
$Cu(CH(CH_3)NO_2)(PPh_3)_2$	**2b**	85	178—179	68.7 (68.9	5.0 5.2	2.2 2.1)	593 (676)
$Cu(C(CH_3)_2NO_2)(PPh_3)_2$	**2c**	63	172—173	69.5 (69.2	5.7 5.4	2.3 2.1)	
$Cu(CH(COCH_3)_2)(PPh_3)_2$	**3a**[b]	92	210—215	71.2 (71.6	5.3 5.4)		
$Cu(CH(COOC_2H_5)_2)(PPh_3)_2$	**3b**[b]	78	176—179	72.5 (72.2	5.9 5.8)		594 (747)
$Cu(CH(COCH_3)COOC_2H_5)(PPh_3)_2$	**3c**[b]	67	127—129	70.3 (70.3	5.7 5.4)		410 (717)
$Cu(CH_2CN)(PPh_3)_2$	**4a**	68	188	72.6 (72.7	5.2 5.1	2.1 2.2)	
$Cu(CH(CH_3)CN)(PPh_3)_2$	**4b**	72	179	72.7 (72.9	5.5 5.4	2.4 2.2)	
$Cu(CH(CN)_2)(PPh_3)_2$	**4c**	78	216	71.9 (71.7	4.6 4.8	4.2 4.3)	
$Cu(CH(CN)COOC_2H_5)(PPh_3)_2$	**5**[b]	84	166—167	70.2 (70.2	5.3 5.2	2.2 2.0)	601 (700)

a) Cryoscopic in benzene. b) Prepared independently by Marsich and Camus and co-workers.[3]

TABLE 2. IR AND NMR SPECTROSCOPIC DATA OF THE COPPER DERIVATIVES OF ACTIVE HYDROGEN COMPOUNDS

Complex	ν(CN) and ν(CO)[a] (cm^{-1})	$\Delta\nu$[b] (cm^{-1})	Relevant NMR signals and assignments[c] (δ, ppm from TMS)
2a	1582	24	5.76 (2H, s, CH_2)$\Delta\delta$=1.43[d]
2b	1580	25	1.95 (3H, d, 6 Hz, CH_3) $\Delta\delta$=0.40, 6.26 (1H, q, 6 Hz, CH) $\Delta\delta$=1.86
2c	1600 1580	55 30	2.16 (6H, s, CH_3) $\Delta\delta$=0.61
3a	1598 1510	*ca.*—110	2.04 (6H, s, CH_3), 5.56 (1H, s, CH)
3b	1643	—92	1.0 (6H, t, CH_3), 4.1 (4H, q, CH_2), 5.12 (1H, s, CH)
3c	1635	*ca.*—100	1.0 (3H, t, CH_3), 2.14 (3H, s, CH_3), 4.0 (2H, q, CH_2), 5.36 (1H, s, CH)
4a	2125	—120	
4b	2100	—140	
4c	2150 2095	—120 —175	
5	2180 1670	—70 —80	0.92 (3H, t, CH_3), 3.72 (1H, s, CH), 3.82 (2H, q, CH_2)

a) In KBr disk. ν(C$\overset{...}{=}$N) for **2a**, **2b**, and **2c**; ν(C=O) for **3a**, **3b**, and **3c**; (C≡N) for **4a**, **4b**, and **4c**; ν(C≡N) and (C=O) for **5**. b) $\Delta\nu=\nu(XY)_{complex}-\nu(XY)_{free}$ (X, Y=C, N, O). c) In $CDCl_3$ for **2a**; in C_6D_6 for the other complexes. d) $\Delta\delta=\delta_{complex}-\delta_{free}$. The triphenylphosphine signals are omitted from the table.

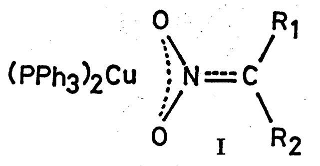


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Fig. 2.

shift towards higher values on complex formation, the new bands appearing in the absorption regions characteristic of the aci-nitroalkanato anion.[7]

In the NMR spectra of the nitroalkanato complexes the α-proton signals of nitromethane and nitroethane are shifted to lower field by 1.44[6] and 1.86 ppm, respectively, and the α-methyl proton signals of nitroethane and 2-nitropropane to the same direction by 0.40 and 0.61 ppm, respectively. Since the protons attached to the carbon directly bonded to copper in alkylcopper complexes give rise to signals at relatively higher fields as compared with those in usual organic compounds,[2b] the low field shift of nitroalkane signals upon bonding to copper is not in line with the substitution of the nitroalkanes by copper at the α-position forming a nitroalkylcopper complexes.

The sp^2 character around the α-carbon in the aci-nitro type complex I accounts for the lowering of the α-proton and α-methyl signals.

Since the nitroalkanato ligand $RCHNO_2$ is considered to be bonded to copper atom through the nitro group, the reaction of the complex with alkyl halide R′X is expected to give *O*-alkylated compound $RCH{=}N(O)OR'$ as in the reactions of copper phenoxide with alkyl halides.[8)] However, the reactions of complexes **2a**, **2b**, and **2c** with alkyl halides give α-*C* alkylated compounds $RCHR'NO_2$, *e.g.*,

$$\mathbf{2b} + CH_3I \xrightarrow[\text{THF}]{\text{r.t.}} \text{2-nitropropane (16\%)}$$

The α-alkylated compounds can be produced through a direct electrophilic attack of R′X at the α-carbon in the aci-nitromethanato ligand or through isomerization of the *O*-bonded species I to the *C*-bonded species.

On allowing complex **2a** to stand in chloroform at room temperature it is decomposed to release nitromethane.[6)] Since employment of $CDCl_3$ does not cause the introduction of D into the nitromethane released, the possibility of the abstraction of hydrogen of chloroform by the nitromethanato ligand is excluded. The PPh_3 ligand coordinated with Cu may give its ortho hydrogen to the nitromethanato ligand with formation of ortho metalized PPh_3 ligand and nitromethane. This type of abstraction of ortho hydrogen of PPh_3 has been observed in the decomposition of $RhCH_3(PPh_3)_3$ in solutions.[9)]

Cryoscopic determination of the molecular weight indicates that the nitroethanato complex has a monomeric structure in benzene with partial dissociation of the PPh_3 ligands.

The ν(C=O) bands assignable to free C=O groups of the β-dicarbonyl compounds (acetylacetone, diethyl malonate, ethyl acetoacetate) disappear on the complex formation with copper, new bands appearing in a lower frequency region which is shifted by *ca.* 100 cm^{-1} from the original ν(C=O). The IR data indicate the formation of an *O,O′*-bonded six-membered chelate β-dicarbonyl ligands, excluding the possible metalization of the β-dicarbonyl compounds through the α-carbon.[10)] In the *C*-bonded complexes the ν(C=O) bonds are usually observed at much higher frequency, 1700—1800 cm^{-1}. The *O,O′*-bonded structure in $Cu(CF_3COCHCOCH_3)(PPh_3)_2$ has been established by X-ray crystallography.[11)] The molecular weight determination of complexes **3b** and **3c** gave lower values than those calculated for each complex suggesting dissociation of one of PPh_3 ligands in benzene.

Some by-products such as the dimers of cyanoalkanes (*e.g.*, 2-aminocrotonitrile from acetonitrile) are formed in the metalization of cyanoalkanes by alkali metals, contamination of the alkali metal cyanoalkanate with the by-products being inevitable.[12)] However, contamination of complexes **4a** and **4b** with the by-products is excluded since each IR spectrum of the complexes shows only a sharp ν(C≡N) band and acidolyses of the complexes with acetic acid give only the parent cyanoalkanes as confirmed by gas chromatography. Appearance of two ν(C≡N) bands in the IR spectrum of **4c** seems to be due to the separation of $\nu(CN)_{sym}$ and $\nu(CN)_{asym}$ vibrations in the dicyanomethanato ligand.

For the metal derivatives of cyanoalkanes the following forms (a)—(e) are conceivable ((c) is possible only when R=H):[12b)]

$$\begin{array}{ccc} \mathrm{MCHR{-}C{\equiv}N}, & \mathrm{MCR{=}C{=}NH}, & \mathrm{MC{\equiv}C{-}NHR}, \\ \text{(a)} & \text{(b)} & \text{(c)} \\ \mathrm{RC{\equiv}C{-}NHM}, & \mathrm{HRC{=}C{=}NM} & \\ \text{(d)} & \text{(e)} & \\ & \mathrm{M = metal} & \end{array}$$

As for complexes **4a** and **4b**, however, the presence of the tautomeric species (b), (c), and (d) is not plausible since their IR spectra show no ν(N–H) band. Insolubility of complexes **4a**, **4b**, and **4c** prevents a detailed structural examination of the complexes by NMR spectroscopy, but form (a) is preferred to the other forms for the present copper derivatives of cyanoalkanes, since some sodium derivatives of cyanoalkanes are known to exist mainly in the *C*-bonded form and the ν(CN) bands of the present copper derivatives appear in the same range of the ν(CN) bands as in the sodium derivatives.[12a)] The insolubility of the complexes in organic solvents (acetone, acetonitrile, tetrahydrofuran, benzene, chloroform *etc.*) suggests that the complexes are aggregated by intermolecular association between the CN group and copper.

In contrast to complexes **4a**, **4b**, and **4c** the copper derivative of the β-carbonyl cyanoalkane, ethyl cyanoacetate, is soluble in common organic solvents. The shift of the α-proton signal of ethyl cyanoacetate to lower magnetic field (NMR) by 0.27 ppm and a relatively large shift of ν(CO) band to lower frequency on the formation of the copper derivative suggest the formation of an *O*- and *NC*-bonded chelate:

The molecular weight determination of complex **5** also excludes the association of the complex through the CN group.

Experimental

General. Preparation and recrystallization of copper complexes were carried out under deoxygenated nitrogen or argon. IR spectra were recorded on a Hitachi Model 295 spectrometer in KBr discs, and ^1H-NMR spectra on a Japan Electron Optics Lab. JNM-PS-100 spectrometer (TMS as an internal standard). The amount of gas evolved was measured by volumetry and the composition of the gas was analyzed with a Hitachi RMU-5B mass-spectrometer and a Shimadzu GC-5B gas chromatograph. The microanalysis of carbon, hydrogen and nitrogen was performed by Mr. T. Saito with Yanagimoto CHN Autocorder Type MT-2. For analytical and spectral data see Tables 1 and 2.

Material. $CH_3Cu(PPh_3)_2(Et_2O)_{0.5}$ **1** was prepared as reported previously.[2)] Solvents were dried by the usual procedure, distilled, and stored under argon or nitrogen. Active hydrogen compounds were purified by distillation brfore use.

Preparations of Copper Derivatives of Nitroalkanes. *Complex 2a*: Nitromethane (3.00 g, 50 mmol) was introduced by a trap-to-trap distillation in a vacuum to complex **1** (100 g, 1.56 mmol) dissolved in tetrahydrofuran (THF, 10 ml). After the mixture had been stirred for 2 h at room temperature a colorless solution was obtained with evolution of methane (35.0 ml, S.T.P., 1.00 mol/Cu). Addition of diethyl ether (20 ml) to the solution and cooling gave white crystlas. They were washed with diethyl ether repeatedly and dried in a vacuum to yield 899 mg of **2a** (1.39 mmol, 89%).

Complex 2b: Nitroethane (3.75 g, 50 mmol) was introduced to a THF (10 ml) solution of complex **1** (1.00 g, 1.56 mmol) in a vacuum. Stirring of the mixture for 2 h at 0 °C gave a colorless solution, releasing a quantitative amount of methane. Addition of diethyl ether (20 ml) to the solution and cooling afforded white crystals. They were recrystallized from THF and dried in a vacuum to give white crystals of **2b** (877 mg, 1.325 mmol. 85%).

Complex 2c: 2-Nitropropane (4.45 g, 50 mmol) was introduced by a trap-to-trap distillation in a vacuum to a THF (10 ml) solution of complex **1** (1.00 g, 1.56 mmol). Stirring the mixture at −20 °C for 2 h gave a light yellow solution with evolution of a quantitative amount of methane. A white solid was precipitated on condensation of the solution and was recrystallized from toluene–diethyl ether. The white crystals were dried in a vacuum to yield 644 mg (63%) of **2c**.

Preparation of Copper Derivatives of β-Dicarbonyl Compounds.

Complex 3a: Acetylacetone (90 mg, 1.00 mmol) was added to a THF (10 ml) solution of complex **1** (640 mg, 1.00 mmol) with a syringe at −78 °C. Stirring of the mixture at −30—0 °C for 2 h gave a colorless solution and methane. The solution was dried up and the residue was recrystallized from THF to give white crystals, which were dried in a vacuum to give 622 mg (92%) of **3a**.

Complex 3b and 3c: Complexes **3b** and **3c** were prepared in a similar way by the reactions of complex **1** 640 mg, 1.00 mmol) with diethyl malonate (160 mg, 1.00 mol) and ethyl acetoacetate (130 mg, 1.00 mmol), respectively (reaction conditions: −30—0 °C, 2 h).

Preparartions of Cyanoalkylcopper Complexes. *Complex 4a*: The reaction of complex **1** (640 mg, 1.00 mmol) with acetonitrils (2.0 g, 49 mmol) in THF (15 ml) at −10°C gradually produced a light yellow precipitate from a dark yellow solution with evolution of methane. After 5 h the precipitate was separated by filtration, washed with THF repeatedly, and dried in a vacuum to yield a pale yellow complex of **4a** (426 mg, 68%).

Complex 4b: Complex **4b** was prepared in the reaction of complex **1** (640 mg, 1.00 mmol) with propionitrile (2.9 g, 36 mmol) in 5 ml of THF solution at room temp. for 5 h. Work-up was carried out in the same way as in the preparation of **4a**. White yellow complex of **4b** (462 mg, yield 72%) was obtained.

Complex 4c: The reaction of complex **1** (1.10 g, 1.72 mmol) with malononitrile (113 mg, 1.72 mmol) in 10 ml of THF solution at −30 °C produced a white precipitate immediately with evolution of a quantitative amount of methane. The precipitate was washed with diethyl ether and THF and dried in a vacuum to yields a white complex of **4c** (870 mg, 78%).

Complex 5: The reaction of complex **1** (640 mg, 1 mmol) with ethyl cyanoacete (113 mg, 1 mmol) in THF solution at −30—0 °C for 2 h produced a colorless solution. The solution was dried up and the residue was recrystallized from diethyl ether and toluene and the crystals were dried in a vacuum to yield white crystals of **5** (582 mg, 78%).

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