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Nuclear Magnetic Resonance Studies of Copper(I) Complexes of Imidazoles. II. Their Reaction with Ethylene, Phosphite, and Isocyanides

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The reaction of binary copper(I) complexes of monodentate imidazole(im) with π acceptor ligands (ethylene, triethyl phosphite, *p*-tolyl isocyanide, and phenyl isocyanide) have been carried out in acetone. The resultant copper(I) complexes have been characterized by ^1H and ^{31}P NMR spectroscopy. Ethylene reacts with $[Cu(im)_2]^+$ (**2**) to give $[Cu(im)_2(C_2H_4)]^+$ (**2-b**), but does not react with $[Cu(im)_3]^+$ (**3**). This shows a clear difference in reactivity between **2** and **3**. Phosphite and isocyanides give rise to a substitution reaction for im in **2** and **3**, accompanying with addition reaction. Among the copper(I) compounds prepared here, two- and four-coordinate forms show sharp ^1H NMR signals of coordinated im, indicating that they are in the slow-exchange regime. This proved that ^1H NMR spectroscopy is a useful tool to characterize diamagnetic copper(I)-imidazole complexes in solution.

Part I of this study[1)] has demonstrated that binary copper(I) complexes of monodentate imidazole (im) are produced quantitatively in acetone at low temperature. Bisimidazolecopper(I) perchlorate, $[Cu(im)_2]ClO_4$ (**2**), and trisimidazolecopper(I) perchlorate, $[Cu(im)_3]ClO_4$ (**3**), are quite interesting in relation to the active site of deoxyhemocyanin,[2,3)] of which copper(I) reacts with π acceptor ligands such as carbon monoxide[4)] and isocyanide.[5)] Furthermore, certain copper(I) complexes provide an ethylene adduct,[6,7)] indicative of a possible receptor[6—8)] of ethylene, which is a plant hormone. From these points of view, knowledge of such coordination chemistry as the coordination number, geometry and reactivity for π acceptor ligands of copper(I)-imidazole systems is important for an intrinsic understanding of the copper(I) active site. This manuscript is concerned with a reaction of **2** and **3** with π acceptor ligands of ethylene, phosphites, and isocyanides and their equilibrium in solution.

Experimental

Materials. Triethyl phosphite was commercially available. Its purity was checked by ^1H and ^{31}P NMR spectroscopy and used without further purification. Phenyl and *p*-tolyl isocyanide were synthesized from corresponding amines.[9)]

Acetone-d_6 (99.8%)(Merck) was utilized as a solvent for ^1H and ^{31}P NMR studies after drying with molecular sieves. High-purity nitrogen (99.9998%) and ethylene (99.9%) were utilized.

$[Cu(im)_2]ClO_4$ (**2**) and $[Cu(im)_3]ClO_4$ (**3**) were prepared according to the method of Part I.[1)] A 2.9×10^{-3} M (1 M=1 mol dm^{-3}) acetone solution of **2** (or **3**) was prepared under nitrogen. While maintaining a nitrogen atmosphere, a stock solution of triethyl phosphite (L) was added to the copper(I) solution in order to vary the ratio of [L]/[Cu]. The mixed solution was stirred for 30 min and then transferred into an NMR sample tube and sealed therein. Ethylene compounds were prepared by passing C_2H_4 gas through a solution of **2** (or **3**).

200 MHz ^1H and 80.79 MHz ^{31}P NMR spectra were obtained as previously described.[1)]

Results and Discussion

Phosphites and isocyanides are good π acceptor ligands.[10)] **2** and **3** react with them to give ternary copper(I) complexes; these are thermally stable, but air-sensitive. Because ternary copper(I) complexes are generally substitution labile, we should find the optimum conditions under which the objective ternary copper(I) complexes predominantly form. Of most significance is the characterization of copper(I) species in solution for the isolation of a copper(I) complex. We have demonstrated[1)] that the ^1H NMR spectra of imidazole give coordination shift that is sensitive to the structure of copper(I) complexes; this indicated that these signals are also applicable to the inquirement of ternary copper(I) complexes in solution.

Reaction with Ethylene. The ^1H NMR spectra at −90 °C of **2** and **3** under ethylene atmosphere were studied as to whether they react with C_2H_4 to give adducts or not. **2** affords an ^1H NMR spectrum, displaying the formation of an ethylene complex (**2-b**), whose chemical shifts are presented in Table 1. **2-b** is thermally stable to a loss of ethylene. Upon the binding of ethylene,[11)] no dissociation of im occured, indicating an addition reaction of ethylene. Monoolefin copper(I) compounds have recently been synthesized: A four-coordinate compound is $[Cu(HB(3,5\text{-}Me_2pz)_3)(C_2H_4)]$,[6a)] ($HB(3,5\text{-}Me_2pz)_3$=hydrotris(3,5-dimethyl-1-pyrazolyl)borate), while a three-coordinate is $[Cu(biL)(C_2H_4)]^+$ (biL=1,10-phenanthroline, 2,2′-bipyridine, etc.).[6b,7)] In analogy with $[Cu(biL)(C_2H_4)]^+$, **2-b** is assigned to $[Cu(im)_2(C_2H_4)]^+$. The reaction of **3** with C_2H_4 is in good contrast with that of **2**. An ethylene atmosphere did not influence the ^1H NMR spectrum of **3** even at −90 °C; this reveals that no formation of $[Cu(im)_3(C_2H_4)]^+$ takes place. The solution of **3** turned blue when C_2H_4 was bubbled at ambient

Table 1. Observed ^{1}H NMR Shifts[a)] of Coordinated Imidazoles of Mixed-Ligand Copper(I) Complexes, $[Cu(im)_nL_m]^+$

L	Coordination No.		1-H	2-H	4-H	5-H
	n	*m*				
Metal-free			13.06	7.97	7.25	7.25
—[b)]	2	0	12.61	8.53	7.42	7.68
—[b)]	3	0	12.41	8.22	7.12	7.59
C_2H_4	2[c)]	1	12.54	8.35	7.28	7.64
$P(OC_2H_5)_3$	2	1	12.56	8.42	7.34	7.64
	2	2	12.46	8.17	7.16	7.56
	3	1	12.59	8.13	7.13	7.54
	1	3	12.48	8.23	7.22	7.59
$CH_3C_6H_4NC$	2	2		8.32	7.31	7.56
	1	3		8.45	7.45	7.63
C_6H_5NC	2	2		8.36	7.30	7.61
	1	3		8.48	7.47	7.65

a) Shift in ppm, from $Si(CH_3)_4$. Error limit, ±0.02 ppm. b) Binary complexes in Ref. 1. c) $[Cu(im)_3]^+$ does not react with C_2H_4.

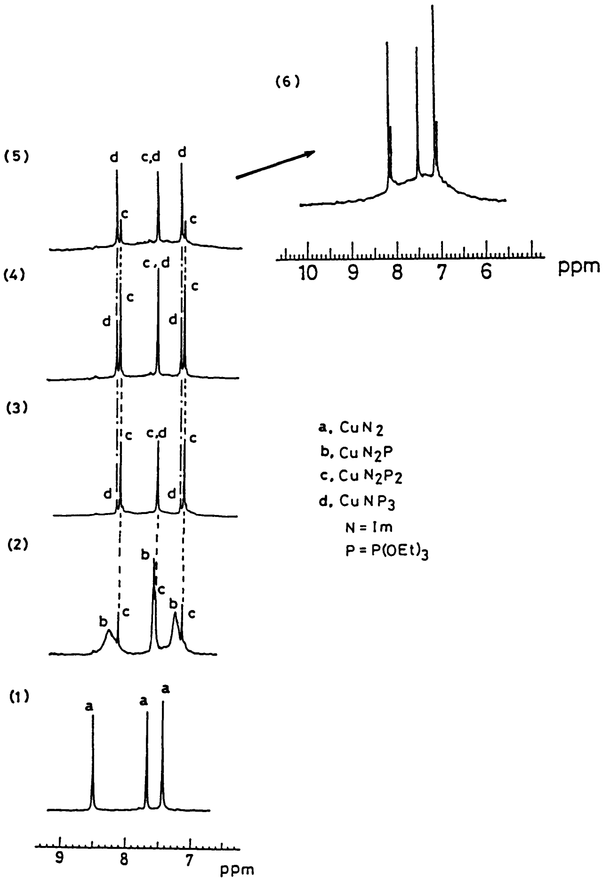
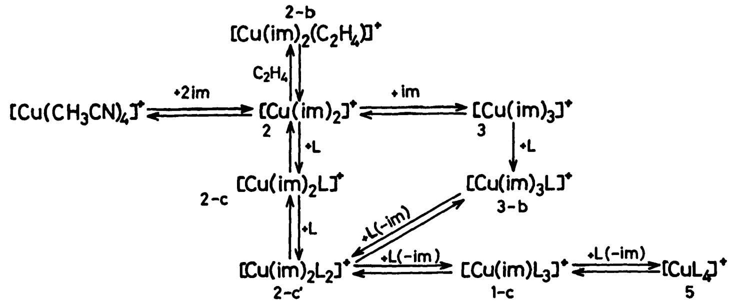


Fig. 1. ^{1}H NMR spectra at −90 °C of acetone-d_6 solution of mixed-ligand copper(I) complexes. Titration of $P(OC_2H_5)_3$ to the solution of **2**. $r=[P(OC_2H_5)_3]/[Cu^+]$: (1) 0; (2) 1.0; (3) 2.0; (4) 3.0; (5) and (6) 4.0. (6) was recorded at wider spectral width than other five spectra in order to examine the base line.

temperature for a long time. The resultant blue species were associated with copper(II) complexes. Hence, it is concluded that **3** does not react with C_2H_4.[12)] In the case of a carbon monoxide atmosphere, thermally very stable $[Cu(im)_3(CO)]^+$ predominantly forms, and gives well resolved ^{1}H NMR signals.[1)] The difference in the reactivity of C_2H_4 and CO against **3** is of much interest in probing the copper(I) active site in a protein.

A four-coordinate complex, $[Cu(HB(3,5\text{-}Me_2pz)_3)(C_2H_4)]$, is in good contrast with $[Cu(im)_3(C_2H_4)]^+$. This pyrazole derivative is stable even in olefin-free solvents, and the prolonged exposure of a solution to an inert atmosphere[6)] is indispensable for removing the coordinated olefin. From this difference in reactivities between these two copper(I) precursors, two factors governing the affinity for C_2H_4 are considered. One is the bonding nature of N donor ligands such as imidazole and pyrazole. The basicity of imidazole is much greater than that of pyrazole. According to the Dewar-Chatt-Duncanson model,[13,14)] the more basic ligand, when it binds copper(I), promotes the π back-bonding of copper(I) and results in stable bonding. Imidazole complexes are more stable than pyrazole complexes as was demonstrated regarding binary copper(I) complexes in Part I.[1)] Such a stability of the binary copper(I) complex is associated with its reactivity with ethylene.

The geometry of a complex is another factor influencing the reactivity of copper(I). Tridentate chelating ligands, especially tripodal ligands, are structurally fixed, being correlated to (1) the hybridization of copper(I) orbitals to form the more stable bond with ethylene, and (2) the controlling the steric interaction between chelating groups and the fourth ligand. $[Cu(HB(3,5\text{-}Me_2pz)_3)]$ has, if present, a trigonal-pyramidal form with copper at an apex. This is indicative of the unusual structure in copper(I) chemistry. In fact, $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2$ is easily dimerized to give $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2$,[15)] revealing that this monomer is very reactive and requires another ligand at the fourth position, giving a tetrahedral complex. In this case, the presence of ethylene as a donor is just appropriate to give a four-coordinate monomer. On the other hand, a structural change might be needed when C_2H_4 binds copper(I) of **3** to give a tetrahedral complex. A number of three-coordinate triangular copper(I) complexes have been found with monodentate ligands. Typical examples are $Na_2[Cu(CN)_3]$,[16)] $[Cu(SPh)_3][BPh_4]_2$ (Ph=phenyl),[17)] and $[Cu(2\text{-methylpyridine})_2]ClO_4$.[18)] According to these facts, **3** at least, has a structure dissimilar to $[Cu(HB(3,5\text{-}Me_2pz)_3)]$, and is supposed to be nearly triangular. The energy barrier on the structural change from a triangular to a tetrahedral form can affect the reactivity of copper(I). It is interesting to



L=phosphite or isocyanide

Scheme 1.

consider the reaction of CO[1] in **3**, where CO readily provides its adduct. Structural factors concerning the affinity for C_2H_4 is significantly associated with the stable formation of four-coordinate ethylene adducts.[19] From this point of view, the systematic synthesis of copper(I) complexes of various tripodal imidazole- or pyrazole- containing chelates is most important in order to elucidate the relationship between the reactivity and structure of three-coordinate imidazole–copper(I) complexes.

Reaction of Phosphite and Isocyanides. We have also utilized triethyl phosphite, phenyl, and *p*-tolyl isocyanide. So long as a high pressure was not provided in the case of ethylene, the concentration was restricted to the solubility at 1 atm. On the contrary, phosphite and isocyanides are available for controlling their concentrations (from high to low) in solution. Typical example of their reaction with binary copper(I) imidazole complexes is presented in Fig. 1. Triethyl phosphite was successively added to a solution of **2** with varying r ($=[P(OC_2H_5)_3]/[Cu]=0$—4). With an increase in r ($0<r<1$), ternary compounds, $[Cu(im)_2(P(OC_2H_5)_3)_n]^+$ ($n=1$ and 2), successively appeared. Copper(I) complexes from two- to four-coordinate have so far been synthesized and characterized.[21] It is to be noted that copper(I) complexes of more than five-coordination hardly form. The further appearance of signals d in Fig. 1 (3)—(5) indicates the occurrence of a substitution reaction at $r>2$. Signals d are attributable to $[Cu(im)(P(OC_2H_5)_3)_3]^+$. $[Cu(im)_2(P(OC_2H_5)_3)_2]^+$ (**2-c′**) and $[Cu(im)(P(OC_2H_5)_3)_3]^+$ (**1-c**) gave sharp signals, indicating that these four-coordinate complexes undergo slow chemical exchanges, while the main signals at the condition $r=1$ are broad. This indicates a partial chemical exchange between **2** and **2-c**. These signals in Fig. 1 were completely assigned in analogy with those illustrated previously for binary and ternary copper(I) complexes.[1]

In order to inquire into the behavior[22] of $P(OC_2H_5)_3$, the ^{31}P NMR spectra of these solutions were measured. A single broad ^{31}P NMR signal at 120±0.5 ppm from $H_3{}^{31}PO_4$ as an external reference was observed at $r<2$ and no metal-free signal of $P(OC_2H_5)_3$ were detected in this region. This indicates that $P(OC_2H_5)_3$ is chemically exchanged among coordinated ones of copper(I) species, as confirmed by the ^1H NMR spectra (Fig. 1). On the other hand, at $r>2$ a quartet signal centered at 127 ppm appeared ($J_{Cu-P}=1180$ Hz), which could be easily assigned to $[Cu(P(OC_2H_5)_3)_4]^+$ (**5**).[23,24] With an increase in r, the ^{31}P signal for ternary copper(I) complexes decreases; it is then covered with the main signal of **5**, and finally disappears. Hence, it is concluded that **5** is a principal species at $r>3$ and that $P(OC_2H_5)_3$ has a high affinity for Cu(I).

At $r>3$, excess metal-free imidazole must be present in solution. However, Fig. 1 (4)—(6) apparently reveal no metal-free signals of imidazole. The wide ^1H NMR spectrum (6 kHz) exhibits a rising baseline at the region 7—9 ppm in Fig. 1 (6). This is averaged broad imidazole signals due to very rapid exchange between the bulk and the coordinated imidazole of binary copper(I) complexes.[25] Imidazoles of **2-c′** and **1-c** are free from this exchange mechanism because their sharp resonances can be simultaneously detected (Fig. 1 (5)). It is important to examine the reactions of **3** in comparison with **2**. The ^1H and ^{31}P NMR spectra were monitored when $P(OC_2H_5)_3$ was also successively added to **3**. As was expected, $[Cu(im)_3(P(OC_2H_5)_3]^+$ (**3-b**) firstly formed with a little broadening. Also, and with an increase in $[P(OC_2H_5)_3]$, **2-c** and **2-c′** appeared, followed by **1-c** and **5**. These facts indicate that the reaction occurring here are all reversible. We can, thus, summarize these reactions in one part of Scheme 1.

In the case of isocyanides, the same trend in ^1H NMR signals as in Fig. 1 has been observed. $[Cu(im)_2L_2]^+$ and $[Cu(im)L_3]^+$ (L=phenyl and *p*-tolyl isocyanide) successively form with the isocyanide addition to **2**. ^1H NMR imidazole signals are sharp enough to resolve various species in solution, denoting the downfield shift more than those in the case of phosphite (Table 1). Phenyl-group signals of isocyanide accidentally collapse with each other; hence, their separations are difficult. Of course, their signal positions are shifted downfield more than those of metal-free species, indicating a coordination to copper(I).

In conclusion, the generated species with C_2H_4 (and CO) are only adduct compounds, while in the case of phosphite and isocyanides, a substitution reaction principally occurs accompanied by a dissociation of imidazole to produce their mono-, bis-, tris-, and finally tetrakis-coordination compounds. The remarkable difference in the reactivity of **2** from **3** is also found in the case of ethylene. Concerning the ^{1}H NMR spectra, four-coordinate mixed-ligand complexes, such as $[Cu(im)_nL_m]^+$ (n=3 and m=1; n=2 and m=2; n=1 and m=3), are in the slow-exchange regime and are readily detected using low-temperature NMR. The lower coordination complexes encounter a chemical-exchange effect to give broad and averaged signals, indicating the labile nature of such complexes.

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11) Acetone solution under ethylene gives single ethylene ^{1}H NMR signal with the intensities much larger than imidazole signals. This reveals the great dissolution of ethylene in acetone. Hence, ethylene ^{1}H NMR signal is averaged due to chemical exchange phenomena, such as

$$Cu(im)_2(C_2H_4)^* + C_2H_4 \rightleftharpoons Cu(im)_2(C_2H_4) + C_2H_4.^*$$

12) Prolonged passing of nitrogen into the solution of **3** changed the colorless solution into pale blue. This blue color solution gave broad ^{1}H NMR imidazole signals, whose intensity is considerably weakened. When the solution of **3** remains for a long time, **3** is oxidized by O_2 contained in nitrogen, or coming from air into synthetic apparatus. Thus, **3** is very sensitive to O_2. On the other hand, CO-passing causes no change in color of the solution even for a long time, indicative of a much better stability against O_2. Under ethylene-passing, a phenomenon similar to the case of nitrogen occurs.

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19) Concerning a steric interaction, the orientation of a coordinated ligand is likely to be important. CO binds Cu(I) in end-on form,[20] while C_2H_4 does in side-on one.[6,7] The latter potentially encounters steric interaction with coordinated imidazole. From this point of view, a tripodal chelate is considered to be a ligand avoiding this type interaction. This can be proved by the use of chelating systems, including these types of stuctural factors.

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22) Triplet methyl and quartet methylene signals of coordinated $P(O(C_2H_5)_3)$ appear near 1 and 4 ppm, respectively. Methylene signals for **2-c**, **2-c′**, and **1-c** collapse with each other; thus, reading their shifts are difficult. Methyl signals of **2-c**, **2-c′**, and **1-c** are 1.24, 1.21, and 1.27, respectively.

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25) The greater [L] becomes, the more **5** forms and metal-free imidazole increases. Under this condition, equilibria are very complicated. In addition to **2-c′** and **1-c**, binary complexes such as **3** also likely to form. Binary ones easily undergo a chemical exchange with metal-free imidazole as was demonstrated in Part I.[1]