

is consistent with previous total emission and magnetic circularly polarized emission results, which have suggested that this ligand binds to the central lanthanide ion in a facial geometry, as opposed to meridional geometry, in the nine-coordinate distorted tricapped prism.²⁶ This alternative method of terdentate binding does not result in enantiomeric structures, and therefore, no CPL would be observed.

Summary

CPL from aqueous solutions of lanthanide ions with multi-dentate achiral ligands excited with circularly polarized light can provide important and unique information concerning the solution structure of the lanthanide complexes that are formed. In general, luminescence experiments yield information concerning the structure of the emitting species at the time of emission, but since in this experiment we are concerned only with the *differential* population in the excited state, our results reflect the kinetic stability of the chiral distribution photoprepared at the time of absorption. The variable emission lifetimes of the lanthanide(III) ions result in a relatively large time window for this type of study, assuming that the solution chemistries of the Ln(III) species are similar. In addition, shielding of Ln(III) by the terdentate ligands

from water molecules leads to relatively high quantum yields. This allowed us to measure CPL from solutions of Sm(III) and Dy(III), which had not been reported previously.

Extensions of this work to include variable-wavelength excitation, temperature-controlled experiments, and comparison of our results with theoretical calculations of 4f-4f optical activity are in progress. It should be possible to obtain relative differential and total emission intensities for both absorptive and emissive transitions by these methods. In addition, an analysis of "mixed-ligand" systems and the effects due to the addition of *chiral* impurity compounds is under way.

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Registry No. Tb(DPA)₃³⁻, 38682-37-0; Eu(DPA)₃³⁻, 38721-36-7; Sm(DPA)₃³⁻, 38682-36-9; Dy(DPA)₃³⁻, 38721-96-9; Dy(ODA)₃³⁻, 58855-72-4; Tb(ODA)₃³⁻, 58855-80-4; Eu(ODA)₃³⁻, 43030-81-5; Sm(ODA)₃³⁻, 102538-37-4; Pr³⁺, 22541-14-6; Sm³⁺, 22541-17-9; Eu³⁺, 22541-18-0; Tb³⁺, 22541-20-4; Dy³⁺, 22541-21-5.

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Studies of Copper(I) Olefin Complexes. Formation Constants of Copper Olefin Complexes with 2,2'-Bipyridine, 1,10-Phenanthroline, and Their Derivatives

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Twenty-five new copper(I) olefin complexes, [Cu(biL)(olefin)]⁺ (biL = the derivatives of 2,2'-bipyridine and 1,10-phenanthroline (phen); olefin = ethylene and derivatives), were synthesized, and the formation constants were determined spectrophotometrically in 0.3 and 0.5 M acetonitrile/ethanol. The influence of substituents of the biL and olefin on the formation constants and the ¹H NMR of the olefinic protons of coordinated ethylene was investigated. The formation constant for the copper ethylene complex (Cu(biL)⁺ + C₂H₄ ⇌ [Cu(biL)(C₂H₄)]⁺) was found to increase with increasing pK_a of biL; electron-donating substituents such as methyl on biL stabilize the ethylene complexes, whereas electron-withdrawing substituents such as Cl destabilize it. ¹H NMR resonances of the olefinic protons of [Cu(biL)(C₂H₄)]⁺ move upfield as the pK_a value of biL increases, indicating an increase in the electron density around the olefinic protons. These findings demonstrate that the σ donation from biL to copper(I) is enhanced as the basicity of biL increases and the resulting electron-rich copper(I) enhances π back-donation in the copper(I)-ethylene bonding. The formation constants of [Cu(phen)(olefin)]⁺ at 25 °C vary from 0.1 to 18 M⁻¹, although they are not as sensitive to the substituent groups on the double bond of the olefin as those of nickel(0) olefin complexes. There is no simple correlation of the formation constant with the Hammett σ, as is distinct from nickel(0) and silver(I) olefin complexes.

Introduction

The binding of unsaturated hydrocarbons to transition metals has occupied a central position in organometallic chemistry¹ in connection with the C=C bond distance,²⁻⁴ activation⁵⁻⁸ coordination

form (upright or in plane),⁹ olefinic proton and carbon NMR of the coordinated olefin,^{10,11} and the formation constant

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of the olefin complex.^{10,12,13} The nature of metal-olefin bonding has been the subject of numerous theoretical studies.^{9,14,15} In addition, of all the transition-metal organometallic reagents developed for application to organic synthesis, organocopper(I) complexes are by far the most often used by the synthetic organic chemist.¹ The Dewar-Chatt-Duncanson concept¹⁶ of olefins being σ donors and π acceptors has been used to explain most of the features observed in olefin bonding and has been shown to be readily applicable to the bonding of other types of unsaturated molecules. The contribution from σ donation to metal-olefin bonding was found to be important for silver(I) olefin complexes, whereas the contribution from π back-donation was found to be important for nickel(0) olefin complexes. We are interested in whether σ donation or π back-donation is dominant in the olefin complexes of copper(I), which has the same isoelectronic structure (d^{10}) as nickel(0) and silver(I). However, little is known about copper-olefin bonding or about the factors that are important in determining the stability of the copper olefin complex.

Ethylene is a plant hormone that causes seeds to sprout, flowers to bloom, fruit to ripen and fall off, and leaves and petals to shrivel and turn brown.¹⁷ The ethylene effect is also manifested by carbon monoxide, acetylene, and olefins with a terminal C=C bond, though their activities are lower.¹⁷ This fact and the requirements of dioxygen for biological activity¹⁸ suggest that a metal ion is present at the ethylene receptor site.¹⁹ Thompson recently reported that the coordination chemistry of copper ethylene complexes is consistent with the proposed role of copper at the

ethylene receptor sites of plants.²⁰ This should draw the attention of bioinorganic chemists to the synthesis, reaction, and structure of copper(I) ethylene complexes which are, in general, thermodynamically unstable and extremely air-sensitive.

In this paper, we synthesized 25 new copper(I) olefin complexes, $[\text{Cu}(\text{biL})(\text{olefin})]^+$, and investigated the influence of substituents on biL and olefin on the formation constants with the aim of elucidating the nature of the copper(I)-olefin bonding, where biL is derivatives of 1,10-phenanthroline and 2,2'-bipyridine.

Experimental Section

General Methods. All operations were carried out under dry, purified nitrogen and ethylene by using the standard Schlenk or vacuum line technique. Tetrakis(acetonitrile)copper(I) perchlorate^{21a} and hexafluorophosphate^{21b} were prepared according to literature procedures. Acetone treated with potassium permanganate was dried over potassium carbonate from 4-A molecular sieves. Acetonitrile was purified according to a literature procedure.²² NMR spectra were obtained in acetone- d_6 with a JEOL FX200 NMR spectrometer. All reported peak positions are relative to tetramethylsilane. Electronic spectra were recorded on Hitachi spectrophotometer. Reagent grade 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and their derivatives were obtained from Wako Pure Chemical, Inc. All other chemicals were of reagent grade and were used without further purification.

Preparation of $[\text{Cu}(4,4'\text{-Me}_2\text{bpy})(\text{C}_2\text{H}_4)]\text{ClO}_4$. Tetrakis(acetonitrile)copper(I) perchlorate (81.8 mg, 0.25 mmol) and 4,4'-Me₂bpy (=4,4'-dimethyl-2,2'-bipyridine) (46 mg, 0.25 mmol) were stirred for 1 h in approximately 5 mL of acetone under ethylene. A white crystalline product precipitated, which was filtered off and dried under ethylene gas. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{CuClO}_4$: C, 44.80; H, 4.31; N, 7.47. Found: C, 44.82; H, 4.68; N, 7.46.

Preparation of $[\text{Cu}(3,4,7,8\text{-Me}_4\text{phen})(\text{C}_2\text{H}_4)]\text{ClO}_4$. Tetrakis(acetonitrile)copper(I) perchlorate (81.8 mg, 0.25 mmol) and 3,4,7,8-Me₄phen (=3,4,7,8-tetramethyl-1,10-phenanthroline) (59 mg, 0.25 mmol) were stirred for 1 h in approximately 5 mL of acetone under ethylene. A white crystalline product precipitated, which was filtered off and dried under ethylene gas. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{CuClO}_4$: C, 50.58; H, 4.73; N, 6.56. Found: C, 50.44; H, 4.95; N, 6.50.

Preparation of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]\text{ClO}_4$. Other ethylene complexes, $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]\text{ClO}_4$, [biL = bpy, phen, 4,4'-diphenyl-2,2'-bipyridine (4,4'-Ph₂bpy), 5-chloro-1,10-phenanthroline (5-Cl(phen)), 2,9-dimethyl-1,10-phenanthroline (2,9-Me₂phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me₂phen), 2-(2-pyridyl)benzimidazole (pbi), di-2-pyridyl ketone (dpk)] were prepared in the same manner as $[\text{Cu}(4,4'\text{-Me}_2\text{bpy})(\text{C}_2\text{H}_4)]\text{ClO}_4$. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{CuClO}_4$ ($[\text{Cu}(\text{bpy})(\text{C}_2\text{H}_4)]\text{ClO}_4$): C, 41.50; H, 3.49; N, 8.07. Found: C, 41.52; H, 3.98; N, 8.06. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{CuClO}_4$ ($[\text{Cu}(4,4'\text{-Ph}_2\text{bpy})(\text{C}_2\text{H}_4)]\text{ClO}_4$): C, 57.71; H, 4.04; N, 5.61. Found: C, 57.67; H, 4.29; N, 5.71. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{CuCl}_2\text{O}_4$ ($[\text{Cu}(5\text{-Cl(phen))}(\text{C}_2\text{H}_4)]\text{ClO}_4$): C, 41.44; H, 2.74; N, 6.91. Found: C, 41.41; H, 2.95; N, 6.90. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{CuClO}_4$ ($[\text{Cu}(2,9\text{-Me}_2\text{phen})(\text{C}_2\text{H}_4)]\text{ClO}_4$): C, 48.12; H, 4.05; N, 7.02. Found: C, 48.15; H, 4.83; N, 7.09. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{CuClO}_4$ ($[\text{Cu}(4,7\text{-Me}_2\text{phen})(\text{C}_2\text{H}_4)]\text{ClO}_4$): C, 48.12; H, 4.05; N, 7.02. Found: C, 48.17; H, 4.21; N, 7.00. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{CuClO}_4$ ($[\text{Cu}(\text{phen})(\text{C}_2\text{H}_4)]\text{ClO}_4$): C, 45.29; H, 3.26; N, 7.55. Found: C, 45.32; H, 3.58; N, 7.53. Calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{CuClO}_4$ ($[\text{Cu}(\text{pbi})(\text{C}_2\text{H}_4)]\text{ClO}_4$): C, 43.53; H, 3.40; N, 10.88. Found: C, 43.59; H, 3.71; N, 10.81. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{CuClO}_4$ ($[\text{Cu}(\text{dpk})(\text{C}_2\text{H}_4)]\text{ClO}_4$): C, 41.61; H, 3.23; N, 7.47. Found: C, 41.70; H, 3.39; N, 7.52.

Preparation of $[\text{Cu}(\text{biL})(\text{olefin})]^+$. Olefin complexes of $[\text{Cu}(\text{biL})(\text{olefin})]^+$ were prepared in 100 mL of acetone by stirring tetrakis(acetonitrile)copper(I) perchlorate (45 mg, 0.25 mmol), biL (0.25 mmole), and olefin (0.25–250 mmol) under N₂. The brown solution of $\text{Cu}(\text{biL})^+$ turned colorless with the complete formation of the olefin complexes.

Determination of the pK_a Value of the Bidentate Ligand. The acid dissociation constant, K_a , of bidentate HbiL^+ (acidic form) is given by eq 1. Both HbiL^+ and biL have strong absorption peaks in the ultra-

$$K_a = [\text{H}^+][\text{biL}]/[\text{HbiL}^+] \quad (1)$$

$$\text{pK}_a = \text{pH} - \log ([\text{biL}]/[\text{HbiL}^+]) \quad (2)$$

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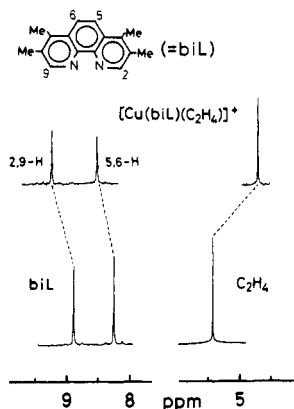


Figure 1. ^1H NMR spectra of 3,4,7,8- Me_4phen , ethylene, and $[\text{Cu}(3,4,7,8\text{-Me}_4\text{phen})(\text{C}_2\text{H}_4)]^+$ in acetone- d_6 at 23 $^\circ\text{C}$.

violet region. The spectrum change interval of pH 2–7 was obtained with buffer solutions. By using the same concentration of biL (5×10^{-5} M for bpy and its derivatives and 2×10^{-5} M for phen and its derivatives in dioxane 1/250 v/v) in each of the measurements at different values of pH and measuring the absorbance for each solution at $\lambda_{\text{max}}(\text{A})$ for the acidic form and $\lambda_{\text{max}}(\text{B})$ for the basic form, we calculated the relative amounts of HbiL^+ and biL in solution from eq 3 and 4, where ϵ_{A} and ϵ_{B}

$$A_{\text{A}} = \epsilon_{\text{A}}(\text{HbiL})[\text{HbiL}^+] + \epsilon_{\text{A}}(\text{biL})[\text{biL}] \quad (3)$$

$$A_{\text{B}} = \epsilon_{\text{B}}(\text{HbiL})[\text{HbiL}^+] + \epsilon_{\text{B}}(\text{biL})[\text{biL}] \quad (4)$$

are molar absorption coefficients at $\lambda_{\text{max}}(\text{A})$ and $\lambda_{\text{max}}(\text{B})$, respectively. Solving these equations gave the ratio $[\text{biL}]/[\text{HbiL}^+]$, and pK_{a} was then obtained with eq 2. The pK_{a} values of 3,4,7,8- Me_4phen and 4,4'- Me_2bpy are 6.58 and 5.39, respectively.

Results and Discussion

Characterization of Copper(I) Ethylene Complexes. White crystalline $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]\text{ClO}_4$ can be isolated from the reaction of tetrakis(acetonitrile)copper(I) perchlorate and biL in acetone under an ethylene atmosphere. The completely dried colorless complex²³ is stable in air for several hours at room temperature. Ethylene exhibits a $\text{C}=\text{C}$ stretching frequency coupled with $\delta_{\text{s}}(\text{CH}_2)$ ²⁴ at 1623 cm^{-1} , whereas the (ethylene)copper(I) complexes with bpy, 4,4'- Me_2bpy , 4,4'- Ph_2bpy , phen, and 2,9- Me_2phen show the stretching frequencies at 1523, 1526, 1525, 1527, and 1537 cm^{-1} , respectively. The $\text{C}=\text{C}$ stretching frequency of ethylene thus decreases 87–100 cm^{-1} with coordination to copper(I). The reported decrease²⁵ in the stretching frequency of ethylene upon coordination is 40 cm^{-1} for $\text{Ag}(\text{C}_2\text{H}_4)^+$, 96 cm^{-1} for $[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$, 103 cm^{-1} for $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$, 107 cm^{-1} for $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$, 120 cm^{-1} for $[\text{Cu}(\text{NH}(\text{py})_2)(\text{C}_2\text{H}_4)]^+$ and 98–118 cm^{-1} for some copper(I) ethylene complexes.^{20d} The decrease in the $\text{C}=\text{C}$ stretching frequency has been thought to correspond roughly to the increase in the π character of the double bond.²⁶ The decrease for the Cu(I) complexes is larger than that of the Ag(I) complex but is similar to those of the Pd(II) and Rh(I) complexes.

^1H NMR spectra of 3,4,7,8- Me_4phen , ethylene, and $[\text{Cu}(3,4,7,8\text{-Me}_4\text{phen})(\text{C}_2\text{H}_4)]^+$ at -90 $^\circ\text{C}$ are shown in Figure 1. The resonances of free 3,4,7,8- Me_4phen at 8.26 ppm (5-H, 6-H) and 8.89 ppm (2-H, 9-H) shifted to 8.53 and 9.24 ppm in the ethylene complex, respectively. Such a downfield shift of the resonances of phen^{20d} and bpy²⁷ is generally observed with coordination to a metal ion. In contrast, the resonance of the olefinic protons of ethylene at 5.44 ppm moves upfield (4.72 ppm) with coordination

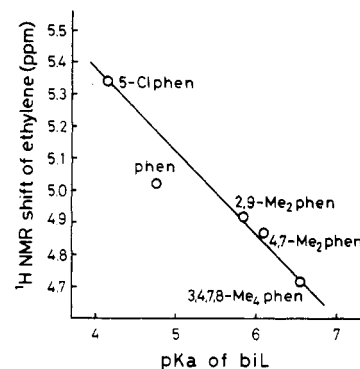
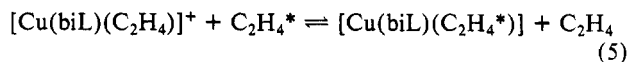


Figure 2. Plot of ^1H NMR chemical shifts of the olefinic protons of ethylene in $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ at -90 $^\circ\text{C}$ against pK_{a} values of biL. The solvent is acetone- d_6 .

to copper(I). This agrees with the trend that olefin π complexation for most transition metals results in shielding of the olefinic protons.^{10,20} The ^1H NMR spectra demonstrate the formation of the ternary copper(I) complex with ethylene and 3,4,7,8- Me_4phen in solution. In the same manner, the other ternary complex formations in solution were confirmed by their ^1H NMR spectra.

NMR Studies of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ in Solution. The ^1H NMR spectrum of ethylene in the acetone- d_6 solution containing free ethylene and $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ gives a single resonance due to rapid chemical exchange.



In this case, the chemical shift observed (δ_{obsd}) is given by

$$\delta_{\text{obsd}} = P_{\text{c}}\delta_{\text{c}} + P_{\text{f}}\delta_{\text{f}} \quad (6)$$

where δ_{c} and δ_{f} (5.44 ppm at -90 $^\circ\text{C}$) are the chemical shifts of complexed and free ethylene, respectively, and P_{c} and P_{f} represent the mole fractions of complexed and free ethylene, respectively. If the dissociation of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ is small, the contribution of the second term $P_{\text{f}}\delta_{\text{f}}$ in eq 6 is negligible. In order to suppress the dissociation of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, the NMR sample solutions at -90 $^\circ\text{C}$ were prepared by dissolving the crystals in ethylene-free solvents and measured.²⁸ The chemical shifts of ethylene protons of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ are summarized in Table I.

All ethylene complexes measured here exhibit shielding (5.34–4.70 ppm) of the olefinic protons, similar to the ethylene complexes of niobium (0.6–1.3 ppm),²⁹ rhodium (1.4–1.9 ppm),³⁰ platinum (2.6–4.7 ppm)^{10b,30b,31} and nickel (1.9–2.0 ppm).^{30b,32} In contrast, only the silver(I) ethylene complex exhibits deshielding (5.7 ppm).^{30b} Figure 2 shows a plot of the chemical shifts of ethylene protons in $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ against the pK_{a} value of biL. Note that the ^1H NMR resonances of the olefinic protons shift upfield with the increase of pK_{a} of biL. Yamamoto et al. have reported that the upfield shift of the olefinic protons of ethyl methacrylate (ema) on coordination increases with the increase of the pK_{a} of PR_3 (=tertiary phosphine) in a series of Ni- $(\text{PR}_3)_2(\text{ema})$ complexes.³³ ^{13}C NMR shifts of olefinic carbons of (olefin) $(\text{PR}_3)\text{Pd}(\eta^5\text{-C}_5\text{H}_5)$ are also correlated with the Hammett σ^+ parameter.³⁴ A plot of the olefinic carbon chemical shifts vs. the Hammett σ_{p} values of X in *trans*-[(olefin) $\text{PtCl}_2(\text{NC}_5\text{H}_4\text{-4-X})$] gives a good linear correlation.³⁵ In these cases, as X becomes

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- (28) The sample solution at room temperature is brown owing to the dissociation of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, i.e. $[\text{Cu}(\text{biL})\text{S}_2]^+$. On the other hand, it is colorless at -90 $^\circ\text{C}$, indicating that the dissociation is negligibly small.
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Table I. Formation Constants of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, ^1H NMR Chemical Shifts of Olefinic Protons, and $\text{C}=\text{C}$ Stretching Frequencies of Coordinated Ethylene of the Copper(I) Complexes

complex	δ_{H}	$\nu_{\text{C}=\text{C}}, \text{cm}^{-1}$	$\text{p}K_{\text{a}}$ of biL	$K_{\text{p}}, \text{atm}^{-1}$	n
C_2H_4	5.44 ^b 5.38 ^c	1623			
$[\text{Cu}(5\text{-Cl}(\text{phen}))(\text{C}_2\text{H}_4)]^+$	5.34 ^b		4.10, 4.07 ^d	2.0 ± 0.1	1.2
$[\text{Cu}(\text{phen})(\text{C}_2\text{H}_4)]^+$	5.02 ^b 5.00 ^c	1525 ^e	4.80, 4.93 ^d	3.9 ± 0.3	1.1
$[\text{Cu}(5\text{-Mephen})(\text{C}_2\text{H}_4)]^+$			5.15, 5.27 ^d	6.8 ± 0.2	1.1
$[\text{Cu}(2,9\text{-Me}_2\text{phen})(\text{C}_2\text{H}_4)]^+$	4.92 ^b	1537	5.84, 5.85 ^d		
$[\text{Cu}(3,4,7,8\text{-Me}_4\text{phen})(\text{C}_2\text{H}_4)]^+$	4.72 ^b		6.58	14.3 ± 0.6	1.1
$[\text{Cu}(\text{bpy})(\text{C}_2\text{H}_4)]^+$	4.84 ^b 4.92 ^c 5.28 ^c	1523 1525 ^e	4.25, 4.42 ^d		
$[\text{Cu}(4,4'\text{-Me}_2\text{bpy})(\text{C}_2\text{H}_4)]^+$	4.75 ^b	1526	5.39	10.5 ± 0.1	1.1
$[\text{Cu}(4,7\text{-Me}_2\text{phen})(\text{C}_2\text{H}_4)]^+$	4.89 ^b		6.09, 5.95 ^d		
$[\text{Cu}(4,4'\text{-Ph}_2\text{bpy})(\text{C}_2\text{H}_4)]^+$	4.89 ^b	1528			
$[\text{Cu}(\text{pbi})(\text{C}_2\text{H}_4)]^+$	4.83 ^b				
$[\text{Cu}(\text{dpk})(\text{C}_2\text{H}_4)]^+$	4.77 ^b				
$[\text{Cu}(\text{NH}(\text{py})_2)(\text{C}_2\text{H}_4)]^+$	4.70 ^f	1505 ^f			
$[\text{Cu}(\text{tmen})(\text{C}_2\text{H}_4)]^+$	4.31 ^c	1525 ^e			
$[\text{Cu}(\text{teen})(\text{C}_2\text{H}_4)]^+$	4.43 ^c	1525 ^e			
$[\text{Cu}(\text{HB}(\text{pz})_3)(\text{C}_2\text{H}_4)] \cdot [\text{CuCl}]$	4.43 ^g				
$[\text{Cu}(\text{HB}(4,5\text{-Me}_2\text{pz})_3)(\text{C}_2\text{H}_4)]$	4.41 ^g				
$[\text{Ni}(\text{P}(\text{O}-\text{o}-\text{tol})_2)_2(\text{C}_2\text{H}_4)]$	1.9 ^h	1487 ^h			
$[\text{RhCp}(\text{C}_2\text{H}_4)_2]$	1.9 ^h	1493 ^h			
$[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)]$	3.1 ^h	1524 ^h			
$[\text{PdCl}_3(\text{C}_2\text{H}_4)]^-$	4.7 ^h	1526 ^h			
$[\text{Ag}(\text{C}_2\text{H}_4)]^+$	5.7 ^h	1583 ^h			

^aIn 0.5 M acetonitrile/ethanol solution, 35 °C. ^b–90 °C. ^c23 °C. ^dSmith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1975; Vol. 2. ^eReference 20d. ^fReference 20c. ^gReference 20b. ^hReference 30b.

more electron withdrawing, the olefinic carbon nuclei are deshielded. These results regarding ^1H and ^{13}C NMR shifts of the olefinic protons and carbons of the ternary nickel(0), palladium(II), and platinum(II) olefin complexes agree with the fact that the olefinic proton resonances of the ethylene in the ternary copper(I) ethylene complexes, $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, move upfield with the increase of the $\text{p}K_{\text{a}}$ of biL.

Salomon and Kochi³⁶ measured the NMR chemical shifts of protons and carbons of cyclic olefins on coordination in a series of their copper(I) complexes. They found that olefins with protons which shift further upfield on coordination show larger upfield shifts of their carbons and concluded that both chemical shifts reflect the degree of Cu–olefin back-donation. Clark and co-workers³⁷ have reported that any π -bonding component reflects in the olefinic shieldings in a series of $\text{CH}_3\text{Pt}(\text{COD})\text{L}$ complexes (where L is Cl^- or a variety of neutral Lewis bases and COD is 1,5-cyclooctadiene). Thus, π back-donation from metal to olefin results in the shielding (upfield shift) of olefinic protons.¹⁶ The result shown in Figure 2, that is, the good correlation of the upfield shifts of ethylene protons with $\text{p}K_{\text{a}}$ of biL in $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, clearly indicates that the σ donation of the nitrogens of biL to copper(I) is enhanced as the nitrogen basicity increases and the resulting electron-rich copper promotes π back-donation in the copper–ethylene bonding. This should be noted to demonstrate the participation of π back-donation in the copper–ethylene bonding but does not mean the relative importance of π back-donation compared with σ donation because the chemical shifts give no detailed information on σ bonding. In fact, σ bonding in copper(I)–ethylene bonding has been shown to predominate,²⁰ as will be described below.

Formation Constants of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$. The formation constants (K_{p}) of the ethylene complexes, $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, given by eq 8 were measured spectrophotometrically, where P is the



$$K_{\text{p}} = [\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)_n^+] / [\text{Cu}(\text{biL})^+] P^n \quad (8)$$

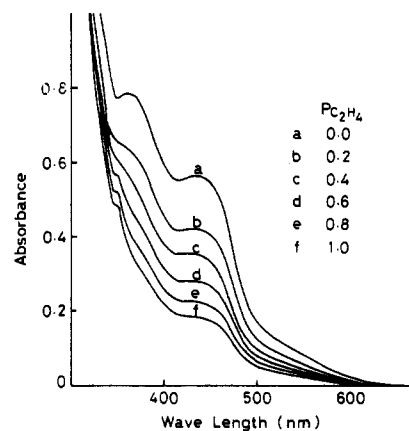


Figure 3. Electronic spectra of $\text{Cu}(\text{phen})^+$ in 0.5 M acetonitrile/ethanol under $\text{C}_2\text{H}_4/\text{N}_2$ at 23 °C. $P_{\text{C}_2\text{H}_4}$ is the partial pressure of C_2H_4 .

partial pressure of ethylene gas. Equation 8 can be written as eq 9, where C_0 and C_x are the initial concentration of $\text{Cu}(\text{biL})^+$

$$K_{\text{p}} = C_x / (C_0 - C_x) P^n \quad (9)$$

and the concentration of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, respectively. A reddish brown solution of $\text{Cu}(\text{biL})^+$ turns colorless with increasing C_2H_4 partial pressure, as shown in Figure 3. The formation constant K_{p} for this system is given by eq 10.^{27a} Here A is the

$$\log R = \log K_{\text{p}} + n \log P \quad (10)$$

$$R = (A - A_c) / (A_0 - A) \quad (11)$$

absorbance at partial pressure P ; A_0 and A_c are the absorbance of $\text{Cu}(\text{biL})^+$ and $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, respectively. The formation constant and coordination numbers n were obtained from the intercept at $P = 1$ and the slope for a linear plot of $\log R$ vs. $\log P$, respectively.

The formation constants of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ are affected by the concentration of acetonitrile (S), as shown in Table II.

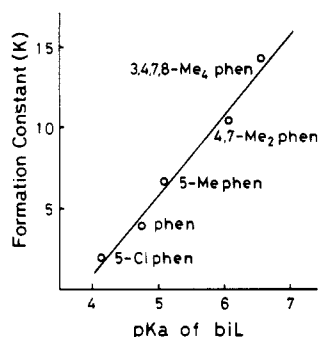
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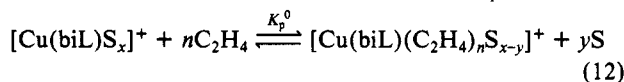
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Table II. Formation Constants of $[\text{Cu}(\text{phen})(\text{C}_2\text{H}_4)]^+$ in Acetonitrile/Ethanol Solution at 35 °C

$[\text{CH}_3\text{CN}]$, M	K_p , atm^{-1}	$K_p[\text{CH}_3\text{CN}]$	$K_p[\text{CH}_3\text{CN}]^2$
0.25	11.3	2.8	0.71
0.30	8.6	2.6	0.77
0.40	5.2	2.1	0.83
0.50	3.9	2.0	0.98
0.65	2.1	1.4	0.89
0.80	1.7	1.4	1.09
1.20	0.89	1.1	1.28
1.40	0.81	1.1	1.59

**Figure 4.** Plot of formation constants (K_p , atm^{-1}) at 35 °C against $\text{p}K_a$ values of biL for $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$. The solvent is 0.5 M acetonitrile/ethanol.

Therefore, eq 5 should be written under the conditions measured as eq 12. The "apparent" formation constant, K_p , and the co-



$$K_p = K_p^0 / [\text{S}]^y \quad (13)$$

ordination numbers of ethylene, n , of seven ethylene complexes $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)_n]^+$ have here measured in 0.5 M acetonitrile/ethanol solution ($[\text{S}] = \text{constant}$)³⁸ and are summarized in Table I. The coordination number n is almost 1 for all complexes measured, indicating the formation of monoethylene complex in solution as well as in the solid state.

Figure 4 shows a plot of the formation constant K_p of $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ against $\text{p}K_a$ values of biL. It is noteworthy that the formation constant increases linearly with increasing $\text{p}K_a$ of biL. This initially demonstrates a relationship between the formation constants and π back-donation in copper-ethylene bonding because it is enhanced with the increase of $\text{p}K_a$ of biL, as described above.

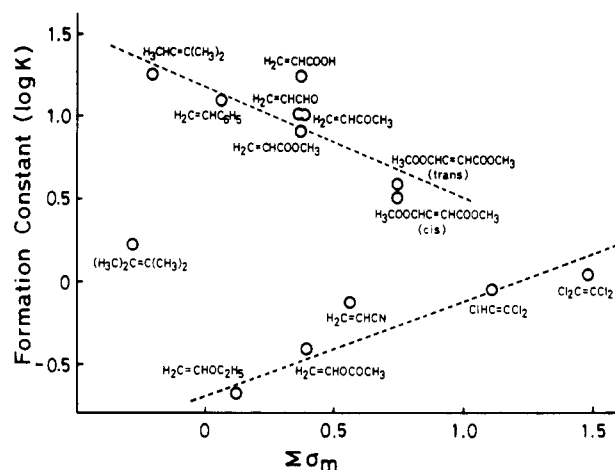
Thompson reported that the carbon-carbon bond distance of the coordinated ethylene of $[\text{Cu}(\text{NHpy}_2)(\text{C}_2\text{H}_4)]\text{ClO}_4$ (1.359 (7) Å),^{20c} $[\text{Cu}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)(\text{C}_2\text{H}_4)]$ (1.329 (9) Å),^{20b} and $[\text{Cu}(\text{HBpz}_3)(\text{C}_2\text{H}_4)] \cdot [\text{CuCl}]$ (1.347 (5) Å)^{20b} is only slightly larger than or essentially the same as the value for free ethylene (1.337 (2) Å),³⁹ and subsequently, σ bonding between the copper(I) and coordinated ethylene is the dominant interaction; π -back-bonding from copper to ethylene is not of great importance. The small π back-bonding ability of copper(I) is also shown by the fact that the upfield shift, -0.10 to -0.72 ppm (from free ethylene), of the olefinic protons of ethylene by coordination to copper(I) in $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$ is small relative to those of nickel(0), -3.48 ppm, and rhodium(I), -2.28 to -3.48 ppm (Table I). Nevertheless, the result shown in Figure 4 demonstrates that the copper(I) ethylene complexes, $[\text{Cu}(\text{biL})(\text{C}_2\text{H}_4)]^+$, are stabilized with even weak π back-bonding as well as σ bonding.

With the solubility⁴⁰ of ethylene in acetone at 25 °C and 1 atm, the approximate formation constant of $[\text{Cu}(\text{phen})(\text{C}_2\text{H}_4)]^+$, K

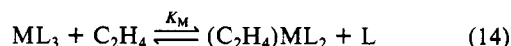
Table III. Stability Constants of Transition-Metal Complexes with Ethylene at 25 °C

M	$\text{M}(\text{C}_2\text{H}_4)$	K , M^{-1}	solvent
$\text{Cu}(\text{phen})^+$	$[\text{Cu}(\text{phen})(\text{C}_2\text{H}_4)]^+$	140	0.3 M CH_3CN /acetone
Ag_{aq}^+	$[\text{Ag}(\text{C}_2\text{H}_4)]^+$	85.3 ^c	H_2O
$\text{Ni}(\text{C}_2\text{F}_4)\text{L}_2^b$	$[\text{NiL}_2(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)]$	235 ± 50^d	benzene
NiL_3^b	$[\text{NiL}_2(\text{C}_2\text{H}_4)]$	$250^{d,f}$	benzene
$\text{RhCl}(\text{PPh}_3)_2$	$[\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$	100 ^e	benzene

^a For $\text{M} + \text{C}_2\text{H}_4 \rightleftharpoons \text{MC}_2\text{H}_4$. ^b $\text{L} = \text{P}(\text{O}-o\text{-tol})_3$. ^c Reference 2b. ^d Reference 13b. ^e Reference 41. ^f $K = [\text{NiL}_2(\text{C}_2\text{H}_4)]/[\text{L}]/[\text{NiL}_3](\text{C}_2\text{H}_4)$.

**Figure 5.** Plot of formation constants at 25 °C against $\Sigma\sigma_m$ for $[\text{Cu}(\text{phen})(\text{olefin})]^+$. The solvent is 0.3 M acetonitrile/ethanol.

($=[\text{Cu}(\text{phen})(\text{C}_2\text{H}_4)]/[\text{Cu}(\text{phen})\text{S}_x][\text{C}_2\text{H}_4]$, of 140 M^{-1} was obtained. The formation constant of the ethylene complexes $[(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)\text{Ni}(\text{P}(\text{O}-o\text{-tol})_3)_2]$,^{13b} $[(\text{C}_2\text{H}_4)\text{RhCl}(\text{PPh}_3)_2]$,⁴¹ and $\text{Ag}(\text{C}_2\text{H}_4)^+$ ^{12b} have been reported to be 235 ± 50 , 100, and 85.3 M^{-1} at 25 °C. It is noted that K for ethylene complexes of Cu(I), Ni(0), Ag(I), and Rh(I) is in the range of 85–235 M^{-1} (Table III). On the basis of ionization potentials of the gaseous d¹⁰ metal atoms (Ni(0), 5.8 eV; Pd(0), ~8.3 eV; Pt(0), ~8.3 eV) and the formation constant K_M of ethylene complexes, $\text{ML}_2(\text{C}_2\text{H}_4)$



nickel(0) has been considered to be a good π donor.⁴² It has been also concluded from the displacement energy of the metal olefin complex that the π character in the silver(I)-olefin bonding is very small.²⁶ The formation constants of the ethylene complexes of d¹⁰ metals increase in the order $\text{Ag(I)} < \text{Cu(I)} < \text{Ni(0)}$, which is the decreasing order in the ionization potentials,⁴³ Ag (21.05 eV) $>$ Cu (20.30 eV) $>$ Ni (5.80 eV); this suggests that π character in copper(I)-ethylene bonding is larger than in silver(I)-ethylene bonding.

Formation Constants of Copper(I) Olefin Complexes. A number of recent papers have dealt with the effect of substituents of olefin on the bonding and physical properties of the coordinated olefins. In a system having an electron-rich metal such as zerovalent nickel, electron-withdrawing substituents on an olefin give more stable olefin complexes, e.g. $[\text{Ni}(\text{P}(\text{O}-o\text{-tol})_3)_2(\text{olefin})]$, with resonance effects being more important than inductive effects.^{13b} Similar results were observed in an iron(0) system.⁴⁴ Reducing the ability of the metal to back-bond in the series $\text{Ni(0)} \geq \text{Pt(0)} > \text{Rh(I)} > \text{Pt(II)} > \text{Ag(I)}$ reduces the importance of resonance and decreases the selectivity of the metal for differently substituted

(38) K_p^0 was not obtained because plots of K_p vs. $[\text{acetonitrile}]^n$ ($n = 1, 2, 3$ or 4) did not give a linear correlation (Table II).

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Table IV. Formation Constants of [Cu(phen)(olefin)]⁺ Complexes in 0.3 M Acetonitrile/Ethanol at 25 °C

olefin	formula	K, M ⁻¹	n ^a
styrene	H ₂ C=CH-C ₆ H ₅	0.13	1.0
trans-stilbene	H ₃ C ₆ -HC=CH-C ₆ H ₅	0.79	0.7
allyl alcohol	H ₂ C=CH-CH ₂ OH	0.28	1.2
acrylonitrile	H ₂ C=CH-CN	1.1	1.0
acrolein	H ₂ C=CH-CHO	11	1.1
acrylic acid	H ₂ C=CH-COOH	18	1.1
methyl acrylate	H ₂ C=CH-COOCH ₃	8.2	1.1
dimethyl fumarate (trans)	H ₃ COOC-CH=CH-COOCH ₃	4.0	1.1
dimethyl maleate (cis)	H ₃ COOC-CH=CH-COOCH ₃	3.3	1.1
maleic anhydride	OOC-CH=CH-CO	5.2	1.0
vinyl acetate	H ₂ C=CHOCOCH ₃	0.40	1.0
ethyl vinyl ether	H ₂ C=CH-OC ₂ H ₅	0.21	1.0
methyl vinyl ketone	H ₂ C=CH-COCH ₃	0.10	1.2
2-methyl-2-butene	H ₃ CHC=C(CH ₃) ₂	0.18	1.1
2,3-dimethyl-2-butene	(H ₃ C) ₂ C=C(CH ₃) ₂	1.68	0.9
trichloroethylene	ClHC=CCl ₂	0.92	1.2
tetrachloroethylene	Cl ₂ C=CCl ₂	1.13	1.2
trans-fumaronitrile	NC-HC=CH-CN	<0.1	

^a Slope for a plot of log *R* vs. log [olefin] (see eq 10, 15).

olefins.^{13b} In a silver(I) system, electron withdrawal destabilized the ethylene complexes and the inductive effect is more important than the resonance effect.¹² The σ -donor properties of the olefin become the dominant feature of the bonding. These results account nicely for an important difference in bonding between nickel(0) to olefin and silver(I) to olefin bonding.

Ours is the first systematic study on the formation constants of copper olefin complexes. Formation constants of copper(I) olefin complexes

$$K = [\text{Cu}(\text{biL})(\text{olefin})_n] / [\text{Cu}(\text{biL})\text{S}_x][\text{olefin}]^n \quad (15)$$

were measured by a method similar to that used for the ethylene complexes, where the [olefin] dimension is not the atmosphere but the molar concentration. The log *R* vs. log [olefin] plot gives a line with slope (=n) nearly equal 1, indicating the formation of a monoolefin complex [Cu(biL)(olefin)]⁺. The formation constants of the complexes obtained are listed in Table IV. One feature of our results, when compared with equilibrium studies on the nickel(0) system, is the insensitivity of the copper(I) formation constant to structural modification of the olefins. The formation constants of [Ni(P(*o*-tol)₃)₂(olefin)] vary over the extremely wide range of 10⁻⁴–4 × 10⁸ M⁻¹ for substituent groups on the double bond,^{13b} whereas the range for the [Cu(phen)(olefin)] system is only 0.1 to 18 M⁻¹. The oxygen next to the double bond in ethyl vinyl ether and vinyl acetate decreases *K* compared with the oxygen in the side chain of allyl alcohol, acrolein, methyl acrylate, dimethyl maleate, and methyl vinyl ketone. The copper(I) olefin complexes with maleic anhydride and trans-fumaronitrile have a small formation constant whereas the nickel olefin complexes exhibit remarkably large formation constants (4.0 × 10⁸ M⁻¹ for maleic anhydride, 1.6 × 10⁸ M⁻¹ for trans-fumaronitrile). The formation constants also appear to be quite insensitive to positional isomerism, as shown by the very similar values of *K* for dimethyl fumarate and dimethyl maleate; the trans isomer is slightly more stable than the cis. The same trend has been observed for the nickel olefin complexes.^{13b} The most striking feature of our results is that a simple correlation of log *K* with the Hammett σ_m or σ_p^+ does not exist in the series of [Cu(phen)(olefin)]⁺, as shown in Figure 5, though the formation constants of nickel(0) and silver(I) olefin complexes correlate well with σ_p^+ and σ_m , respectively. Electron withdrawal destabilizes the copper complexes of the olefins having CH₃, CHO, COCH₃, or COOCH₃ as the substituent group on the double bond, excepting 2,3-dimethyl-2-butene.⁴⁵ On the other hand, electron withdrawal stabilizes the complexes of the olefins having OC₂H₅, OCOCH₃, CN, or Cl.⁴⁶ This indicates that copper(I)-olefin

bonding is stabilized with σ donation and/or π back-donation and the bonding nature is intermediate between those of nickel(0) and silver(I), thus supporting the amphoteric nature.

Conclusion

The results of these studies on ternary copper(I) ethylene complexes indicate that the basicity of the ligand is important in determining the stability of the ethylene complex because π back-donation in copper-ethylene bonding is promoted with increasing basicity. The coordination of an amine of strong basicity to copper(I) may be more advantageous for stabilizing, at least thermodynamically, the ethylene complex than the pyridyl group. In fact, the olefinic protons of ethylene of copper(I) ethylene complexes with tetramethylethylenediamine and tetraethylethylenediamine exhibit ¹H NMR resonances at 4.31 and 4.43 ppm,^{20d} respectively, which are more upfield than those (5.34–4.70 ppm) in [Cu(biL)(C₂H₄)]⁺ and indicate promotion of π back-donation in the copper-ethylene bonding. On the other hand, a copper complex with an amine generally possesses a lower redox potential (Cu^I/Cu^{II})⁴⁷ than a copper complex with pyridine, and subsequently the coordination of amine to copper(I) decreases the stability of the copper(I) ethylene complex as well as the amine complex itself toward O₂ oxidation. Thus, both the thermodynamic stability and the stability for O₂ oxidation must be considered to improve the copper(I) complexes as models of ethylene binding sites of plant tissues that have extremely small dissociation constants (~10⁻¹⁰ M) in the presence of O₂.⁴⁸

The C=C bond distance of coordinated ethylene and the reactivity for carbon monoxide suggest that σ bonding between Cu(I) and coordinated olefin is the dominant interaction and the π -back-bonding ability is poor relative to that of nickel(0).²⁰ The results of these studies also show that the ability of a d¹⁰ metal to π back-bond decreases in the order Ni(0) > Cu(I) > Ag(I), and copper(I) is insensitive to substituent groups on the double bond of the olefin when compared to the case of nickel(0). However, it is emphasized that the weak π back-donation of copper(I) as well as the σ donation is an important factor which stabilizes the olefin complex. This amphoteric nature of copper(I) is supported by the results of theoretical studies that the contribution from σ donation to the methyl-ethylene bonding energy is equally important for all three ethylene complexes of Cu(I), Ag(I), and Au(I), whereas the contribution from π back-donation is important for only the copper(I) ethylene complex.^{9a}

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(45) The small formation constant of 2,3-dimethyl-2-butene may be attributable to the steric effect of four methyl groups. If 2-methyl-2-butene is coordinated to copper mainly with the 3-carbon, the steric effect may be small.

(46) A plot of log *K* vs. σ_p also exhibits the same trend.

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