J. Am. Chem. Soc. 1983, 105, 3522-3527

Copper(I)-Olefin Complexes. Support for the Proposed Role of Copper in the Ethylene Effect in Plants[†]

Jeffery S. Thompson,* Richard L. Harlow, and John F. Whitney

Contribution from the E. I. du Pont de Nemours and Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898.

Received September 20, 1982

Abstract: The synthesis, spectroscopy, and structure of a series of Cu(I)–monoolefin complexes, which show the tight binding of monoolefins characteristic of the ethylene receptor site of plants, are presented. Complexes of the formulation $Cu(HB(3,5\text{-}Me_2pz)_3)(C_2H_4)$ and $Cu(HBpz_3)(olefin)\cdot CuCl$ (olefin = ethylene, propylene, and cyclohexene), where $HB(3,5\text{-}Me_2pz)_3$ and $HBpz_3$ are hydrotris(3,5-dimethyl-1-pyrazolyl)borate and hydrotris(1-pyrazolyl)borate, respectively, were characterized analytically and spectroscopically. The two ethylene complexes were also characterized by single-crystal X-ray diffraction techniques. The complex $Cu(HB(3,5\text{-}Me_2pz)_3)(C_2H_4)$ crystallizes in the monoclinic space group, C_{2h}^5-$P2_1/c$, with four molecules in a unit cell of dimensions a = 13.607 (2) Å, b = 7.781 (2) Å, c = 19.155 (3) Å, and β = 111.10 (1)° at −100 °C. Least-squares refinement of 315 variables has led to a value of the conventional R index (on F) of 0.038 and of R_w of 0.046 for 2223 reflections having $F_o^2 > 2\sigma(F_o^2)$. The geometry about the Cu(I) ion, which is coordinated to three 3,5-dimethylpyrazole nitrogen atoms and an ethylene molecule, is distorted tetrahedral. The carbon–carbon bond distance of the coordinated ethylene molecule is 1.329 (9) Å. The complex $Cu(HBpz_3)(C_2H_4)\cdot CuCl$ crystallizes in the monoclinic space group C_{2h}^5-$P2_1/n$ with four molecules per unit cell of dimensions a = 13.355 (2) Å, b = 12.460 (2) Å, c = 9.145 (2) Å, and β = 92.45 (1)° at −100 °C. Least-squares refinement of 246 variables has led to a value of the conventional R index (on F) of 0.031 and of R_w of 0.029 for 2692 independent reflections having $F_o^2 > 2\sigma(F_o^2)$. The geometry about one of the Cu(I) ions, which is coordinated to two pyrazole nitrogen atoms and an ethylene molecule, is trigonal planar, whereas the geometry about the second Cu(I) ion, which is coordinated to the third pyrazole ring and a chloride ion, is linear. The carbon–carbon bond distance of the coordinated ethylene molecule is 1.347 (5) Å. These complexes demonstrate for the first time that Cu(I)–ethylene coordination chemistry is consistent with the proposed role of copper at the ethylene binding site of plants.

Ethylene is a plant hormone that plays a critical role in virtually every phase of development in most plants: germination, growth, sex expression, fruit ripening, senescence, and abscission.[1–7] Carbons 3 and 4 of methionine appear to be the most important source of the gas in vivo.[1,7] The ethylene effect can be induced by exogenously applied gas as well as by structural analogues of ethylene (compounds with terminal unsaturation).[1–4] Half-maximal activity, determined by the inhibition of growth of pea seedlings, is attained with concentrations of ethylene as low as 0.1 μL/L.[1a] Propylene, 1-butene, acetylene, and carbon monoxide are competitive with ethylene and will also produce the ethylene effect, although significantly higher concentrations are required.[1,5] Biological activity is reduced by molecular size and electron-withdrawing substituents; the relative ethylene effect decreases along the series ethylene, propylene, vinyl chloride, carbon monoxide, acetylene, and 1-butene. Ethane, propane, and 2-butene have no detectable ethylene effect.[1–7]

Although the effects of ethylene on plant processes are well established, the site of ethylene action is not known. The structural requirements for biological activity of olefins and acetylenes and, in particular, the activity of carbon monoxide suggest that a metal ion is present at the ethylene receptor site.[1c,3] Further evidence for the role of a metal ion is the inhibition of olefin binding by dithiocarbamate in a cell-free system from mung beans.[8] A consideration of these properties and the general organometallic chemistry of biologically important transition metals led to the suggestion of a copper ion at the ethylene binding site.[4i] A role for copper has also been suggested in the metabolism of ethylene to ethylene oxide and other products.[4h]

In this contribution, we present the synthesis, spectroscopy, and structure of a series of Cu(I)–monoolefin complexes that show the tight binding of olefin characteristic of the native systems and demonstrate that Cu(I)–olefin coordination chemistry, particularly with ethylene, is consistent with the proposed role of copper at the ethylene receptor site. The compounds reported here are stable to loss of olefin in the absence of excess olefin and have been characterized analytically and spectroscopically; in addition, two ethylene complexes have been characterized by X-ray diffraction methods. In contrast, Cu(I) halide adducts with ethylene and other biologically active monoolefins prepared previously lose olefin readily and have been only poorly characterized.[9,10] Generally,

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[†] Contribution No 3005.

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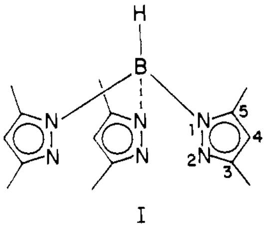
0002-7863/83/1505-3522$01.50/0

excess olefin is needed to stabilize the adducts.[9] Similar results have been obtained for a Cu(I)–ethylene complex with a tridentate amine ligand, although a 1-hexene complex with this ligand has been structurally characterized.[9h] The ligands used in this study, hydrotris(3,5-dimethyl-1-pyrazolyl)borate, HB(3,5-$Me_2pz)_3$ (I), and hydrotris(1-pyrazolyl)borate, $HBpz_3$ (II),[11] were chosen to approximate the binding site typically found or suggested for cuprous ions in metalloproteins.[12] These ligands, which have been used to prepare active-site approximations of several copper proteins,[13,14] provide imidazole-like ligands while restricting the mode of coordination of these groups.



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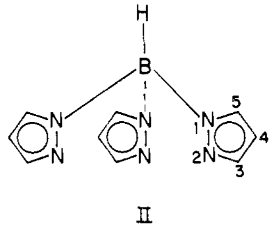

II

Experimental Section

General Methods. All chemcials were reagent grade and were used as received, unless otherwise noted. The solvents dichloromethane, diethyl ether, hexamethyldisiloxane, tetrahydrofuran, and cyclohexene were deaerated with prepurified nitrogen and stored over molecular sieves (4A), which were activated prior to use by heating at approximately 250 °C under high vacuum for several days and then stored under nitrogen. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate and potassium hydrotris(1-pyrazolyl)borate were prepared according to literature procedures.[11] Standard glovebox and Schlenk-ware techniques were used in the handling of air-sensitive complexes. Elemental analyses were performed by the Microchemical Analysis Laboratory, Physical and Analytical Division, Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, DE, and by Galbraith Laboratories, Inc., Knoxville, TN. Samples were handled and stored under a nitrogen atmosphere. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. NMR spectra were obtained in deuteriodichloromethane with a Perkin-Elmer EM-390 spectrometer; all reported peak positions are relative to tetramethylsilane. Gas chromatography was performed with a Perkin-Elmer Sigma 2 gas chromatograph with a 10 ft × $^1/_8$ in. stainless steel column packed with 10% Carbowax 20 M on 80/100 Chromosorb W Aw.

Preparation of [Hydrotris(3,5-dimethyl-1-pyrazolyl)borato](ethylene)copper(I), Cu(HB(3,5-$Me_2pz)_3)(C_2H_4)$ (III). Cuprous iodide (0.35 g, 1.8 mmol) was stirred in approximately 10 mL of dichloromethane under an ethylene atmosphere for approximately 1 h. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate (0.50 g, 1.5 mmol) was added as a powder over 0.5 h. The reaction mixture was stirred under ethylene for 0.5 h and then filtered under nitrogen pressure. The solution volume was reduced to several milliliters with ethylene. White crystalline product was obtained by vapor diffusion of diethyl ether into this solution at −40 °C. Anal. ($C_{17}H_{26}BCuN_6$) C, H, N. IR (cm^{-1}) 3125 w, 3090 w, 2505 m, 1545 s, 1415 s, 1345 s, 1255 m, 1195 s, 1185 s, 1150 w, 1115 w, 1065 s, 1040 m, 980 m, 912 m, 845 m, 808 s, 795 m, 785 m, 720 w, 695 m, 648 w; NMR (ppm) 5.68 (s, 3 H), 4.41 (s, 4 H), 2.30 (s, 9 H), 2.18 (s, 9 H).

Table I. Crystal Data for Cu(HB(3,5-$Me_2pz)_3)(C_2H_4)$ (III) and $Cu(HBpz_3)(C_2H_4)\cdot CuCl$ (IV)

	III	IV
mol for	$C_{17}H_{26}BCuN_6$	$C_{11}H_{14}BClCu_2N_6$
mol wt	388.79	403.62
a, Å	13.607 (2)	13.355 (2)
b, Å	7.781 (2)	12.460 (2)
c, Å	19.155 (3)	9.145 (2)
β, deg	111.10 (1)	92.45 (1)
V, $Å^3$	1892.1	1520
Z	4	4
space group	C_{2h}^5-$P2_1/c$	C_{2h}^5-$P2_1/n$
radiation	Mo Kα (λ 0.710 69 Å) from graphite monochromator	Mo Kα (λ 0.710 69 Å) from graphite monochromator
2θ limits, deg	4–55	4–55
temp, °C	−100	−100
abs coeff, cm^{-1}	12.12	30.76
transmission factor	0.6507–0.8937	0.832–0.999
unique data used ($F_o^2 > 2\sigma(F_o^2)$)	2223	2692
no. of variables	315	246
R	0.038	0.031
R_w	0.046	0.029

Preparation of Chloro[hydrotris(1-pyrazolyl)borato](ethylene)dicopper(I), $Cu(HBpz_3)(C_2H_4)\cdot CuCl$ (IV). Cuprous chloride (0.30 g, 3.0 mmol) was stirred overnight in approximately 10 mL of dichloromethane under an ethylene atmosphere. Potassium hydrotris(1-pyrazolyl)borate (0.40 g, 1.6 mmol) was added as a powder or as a dichloromethane solution (5 mL) over 0.5 h. The reaction mixture was stirred under ethylene for approximately 0.5 h and then filtered under nitrogen pressure. The solution volume was reduced to several milliliters with ethylene. White crystalline product was obtained by either addition of diethyl ether or addition of hexamethyldisiloxane followed by further reduction in volume and cooling to −40 °C. Anal. ($C_{11}H_{14}BClCu_2N_6$) C, H, N. IR (cm^{-1}) 3140 w, 3115 w, 2465 m, 2415 w, 1730 w (br), 1505 w, 1500 s, 1430 s, 1305 s, 1295 s, 1255 w, 1225 s, 1212 s, 1200 m, 1192 s, 1140 w, 1135 s, 1125 s, 1092 m, 1080 m, 1065 s, 1055 s, 1045 s, 975 w, 968 m, 935 w, 920 w, 885 w, 880 w, 850 w, 790 w, 775 w, 765 s, 740 m, 720 s, 655 m, 620 m; NMR (ppm) 7.70 (d, 3 H), 7.55 (d, 3 H), 6.26 (t, 3 H), 4.43 (s, 4 H).

Preparation of Chloro[hydrotris(1-pyrazolyl)borato](propylene)dicopper(I), $Cu(HBpz_3)(C_3H_6)\cdot CuCl$ (V). The procedure described above for the preparation of the ethylene complex IV was used to prepare the analogous propylene complex V, which was isolated as a white, microcrystalline product from a dichloromethane–diethyl ether mixture at −40 °C. Anal. ($C_{12}H_{16}BClCu_2N_6$) C, H, N. IR (cm^{-1}) 3135 w, 3120 w, 3110 m, 2460 m, 2420 w, 1532 w, 1510 m, 1505 m, 1405 s, 1400 s, 1308 s, 1298 m, 1255 w, 1245 w, 1225 s, 1210 s, 1205 s, 1195 m, 1115 s, 1085 m, 1065 s, 1055 s, 1040 m, 985 m, 945 w, 935 w, 925 w, 910 w, 890 w, 855 w, 795 w, 775 s, 765 s, 725 s, 718 s, 660 w; NMR (ppm) 7.71 (d, 3 H), 7.50 (d, 3 H), 6.29 (t, 3 H), 5.3 (m under solvent peak; in acetone-d_6), 4.35 (unsym t, 2 H), 1.70 (d, 3 H).

Preparation of Chloro[hydrotris(1-pyrazolyl)borato](cyclohexene)dicopper(I), $Cu(HBpz_3)(C_6H_{10})\cdot CuCl$ (VI). Cuprous chloride (0.30 g, 3.0 mmol) was stirred for 1 h in 5 mL of dichloromethane and 5 mL of cyclohexene. Potassium hydrotris(1-pyrazolyl)borate (0.40 g, 1.6 mmol) in 5 mL of tetrahydrofuran was added over 0.5 h. The mixture was stirred for an additional 0.5 h and then filtered under nitrogen pressure. Cyclohexene was added until the solution became cloudy. A white crystalline product precipitated upon cooling to −40 °C. Anal. ($C_{15}H_{20}BClCu_2N_6$) C, H, N. IR (cm^{-1}) 3135 w, 3120 w, 3115 w, 3095 w, 2450 m, 2420 w, 1510 m, 1505 m, 1390 s, 1345 w, 1335 w, 1305 s, 1295 m, 1225 ms, 1205 s, 1195 s, 1125 s, 1115 s, 1098 w, 1085 w, 1078 w, 1065 s, 1055 s, 992 w, 982 m, 965 wm, 925 w, 895 w, 878 w, 850 w, 788 m, 762 s, 758 s, 742 w, 725 s, 715 s, 670 w, 660 m, 655 m, 625 m, 620 m; NMR (ppm) 7.65 (d, 3 H), 7.50 (d, 3 H), 6.78 (t, 3 H), 5.47 (s, 2 H), 2.07 (br m, 4 H), 1.50 (br m, 4 H).

X-ray Data Collection and Structure Solution and Refinement for Cu(HB(3,5-$Me_2pz)_3)(C_2H_4)$ (III). Crystals of Cu(HB(3,5-$Me_2pz)_3)(C_2H_4)$ suitable for diffraction studies were obtained by vapor diffusion of diethyl ether into an ethylene-saturated dichloromethane

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solution of III at -40 °C. The crystal chosen was encapsulated in a glass capillary under a nitrogen atmosphere. The crystal was then placed on a Syntex P3 diffractometer and shown to be suitable for diffraction on the basis of ω scans, which showed the peak width at half-height to be ca. 0.40° at -100 °C. The cell parameters were then refined on the basis of 49 computer-centered reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table I.

Intensity data were collected by the standard θ–2θ technique with 1° scan range and a scan rate of 4.0–10.0°/min (total background time equals scan time). During the data collection, four standard reflections were collected after every 200 reflections. There was no significant variation of the intensities during the data collection. The intensities of several reflections were measured at 10° increments about the diffraction vector. Empirical corrections for absorption thereby derived were subsequently applied. The data were processed by using counting statistics and a p value of 0.02 to derive standard deviations.[15]

All crystallographic calculations were performed on a Digital Equipment Corp. VAX 11/780 computer using a system of programs developed by Dr. J. C. Calabrese, Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, DE. The copper atom was located by direct methods. The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinement. In the least-squares refinements, the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where $w = 1/\sigma^2(F_o)$. Atomic scattering factors were taken from Cromer and Waber's tabulation.[16a] Anomalous dispersion terms were those of Cromer.[16b] After convergence of the non-hydrogen portion of the molecule in which the atoms were refined anisotropically, the hydrogen atoms of the HB(3,5-$Me_2pz)_3$ group were located in a Fourier difference synthesis and refined satisfactorily; the hydrogen atoms of the ethylene molecule could not be located. Least-squares refinement converged to $R = 0.038$ and $R_w = 0.046$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - F_c|)^2/\sum wF_o]^{1/2}$. The final difference map shows electron densities 1.13, 0.46, 0.38, and 0.32 e/Å^3 in the vicinity of the ethylene carbon atoms. All other peaks were less than 0.29 e/Å^3 in height. The thermal parameters of the ethylene carbon atoms, C(1) and C(2) (Table II), were found to be unusually large. All attempts to refine the ethylene hydrogen atoms failed. The ethylene group appears to sit in a pocket with a fair amount of vibrational freedom.

The final positional and thermal parameters of the refined atoms appear in Table II.[17] General temperature factors appear in Table III.[17] Tables of the structure amplitudes (Table IV) and a complete listing of bond distances and angles (Table V) are available.[17]

X-ray Data Collection and Structure Solution and Refinement for Cu(HBpz$_3$)(C$_2$H$_4$)·CuCl (IV). Crystals of Cu(HBpz$_3$)(C$_2$H$_4$)·CuCl (IV) suitable for diffraction studies were obtained by vapor diffusion of diethyl ether into an ethylene-saturated dichloromethane solution of IV at -40 °C. The crystal chosen was encapsulated in a glass capillary under a nitrogen atmosphere. The crystal was then placed on a Syntex P3 diffractometer and shown to be suitable for diffraction on the basis of ω scans, which showed the peak width at half-height to be ca. 0.26° at -100 °C. The cell parameters were then refined on the basis of 50 computer-centered reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table I.

Intensity data were collected by the ω-scan technique with a scan range of 1.0° and a scan rate of 4.0–10°/min (total background time equals scan time). Intensity measurements of standard reflections, empirical corrections for absorption, and data processing were performed as described above.

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of programs supplied by the Enraf-Nonius Corp.[18] The copper atom was located by direct methods (MULTAN series). The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinement. The function minimized in the least-squares refinement and the source of atomic scattering factors[16a] and anomalous dispersion terms[16b] are described above. After convergence of the non-hydrogen portion of the molecule, in which the atoms were refined anisotropically, all hydrogen atoms were located in a Fourier difference synthesis and were refined satisfactorily. Least-squares refinement converged to values of $R = 0.031$ and $R_w = 0.029$, where R and R_w are as defined above. All peaks in the final difference Fourier map were less than 0.36 e/Å in height.

The final positional and thermal parameters of the refined atoms appear in Table VI.[17] General temperature factors appear in Table VII.[17] Tables of the structure amplitudes (Table VIII) and a complete listing of bond distances and angles (Table IX) are available.[17]

Results

Synthesis and Properties. The synthesis of Cu(I)–olefin complexes with I and II is straightforward and is presented in eq 1 and 2. (In eq 2: IV, olefin = ethylene; V, olefin = propylene;

$$\mathrm{CuI} + \mathrm{C_2H_4} \xrightarrow{\mathrm{CH_2Cl_2}} \xrightarrow{1} \underset{\mathrm{III}}{\mathrm{Cu(HB(3,5\text{-}Me_2pz)_3)(C_2H_4)}} + \mathrm{KI} \qquad (1)$$

$$\mathrm{2CuCl} + \text{olefin} \xrightarrow{\mathrm{CH_2Cl_2}} \xrightarrow{11} \mathrm{Cu(HBpz_3)(olefin){\cdot}CuCl} + \mathrm{KCl} \qquad (2)$$

VI, olefin = cyclohexene). These preparations take advantage of the well-established property of cuprous halides to form adducts with olefins.[9] These adducts are unstable without excess olefin and were not isolated; rather, the potassium salt of the pyrazolylborate ligand was added. Excess cuprous halide was used for III. Both the halides and the initial olefin adducts are insoluble in dichloromethane, whereas the olefin complexes III–VI are very soluble in this solvent. We found it necessary to add the ligand to the reaction mixture slowly; otherwise, the Cu(I)–polypyrazolylborate dimers (Cu$_2$L$_2$, L = I, II)[13] were formed in significant amounts. The dimers were also isolated as the major product when [Cu(CH$_3$CN)$_4$]ClO$_4$ was used as starting material in the synthesis of IV–VI, when displacement of carbon monoxide from CuL(CO) (L = I, II) with olefin was attempted, and when stoichiometric amounts of CuCl and II were used in the preparation of IV–VI. The propylene and cyclohexene analogues of III could not be prepared by the method indicated in eq 1, presumably because of the steric bulk of the methyl group in the 3-position of the pyrazole rings. The effects of these methyl groups on the properties of coordinated metal ions have been described for other systems.[13,14,19] The pocket formed by these groups around the metal ion is evident from the structural study of III (vide infra). There was no evidence for coordination of propylene or cyclohexene in either solution or the solid state. When these olefins were substituted for ethylene, the Cu(I) dimer Cu$_2$L$_2$ (L = I)[13] was the only isolated product.

The procedures outlined in eq 1 and 2 allow the preparation of white, crystalline compounds whose analytical, spectroscopic, and physical properties are consistent with the indicated formulations. Unlike the majority of previously reported Cu(I)–monoolefin adducts,[9] acceptable elemental analyses were obtained for III–VI without storage of the compounds in the presence of excess olefin.[20] The infrared and NMR spectra of these complexes are also consistent with the indicated formulations and are typical of Cu(I)–polypyrazolylborate complexes (vide infra).[13,14,21] Crystalline compounds appear to be indefinitely stable to loss of olefin in a nitrogen atmosphere. The solids can be dissolved in olefin-free solvents without significant decomposition, as evidenced

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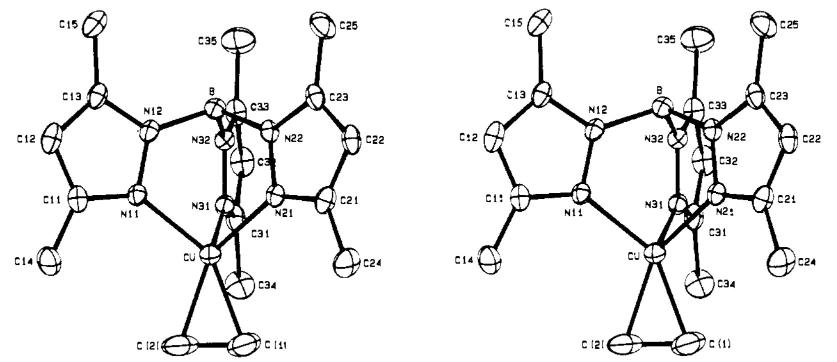

Figure 1. Stereoview of Cu(HB(3,5-Me$_2$pz)$_3$)(C$_2$H$_4$) (III). The vibrational ellipsoids are drawn at the 50% level here and in subsequent figures. The hydrogen atoms have been omitted for clarity. Atom labels are included.

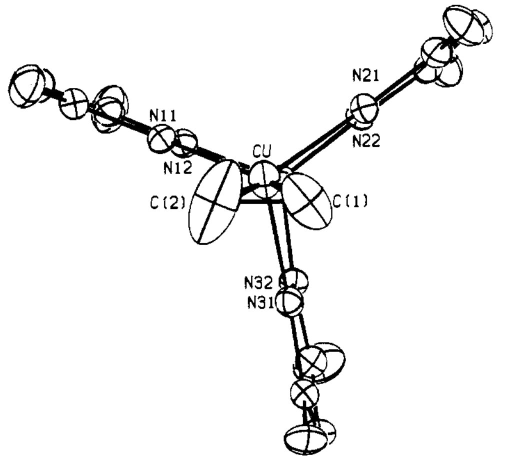

Figure 2. View of Cu(HB(3,5-Me$_2$pz)$_3$)(C$_2$H$_4$) (III) along the Cu–B vector.

by the lack of decomposition products (dimers) in the NMR spectra. The coordinated olefin can be removed by evacuation, diffusion from solution on prolonged exposure to an inert atmosphere, and addition of carbon monoxide or triphenylphosphine. All solutions of the olefin complexes react rapidly with the ambient atmosphere to yield dark green Cu(II) oxidation products, which have not yet been fully characterized but which give rise to EPR spectra typical of Cu(II)–polypyrazolylborate complexes.[14] No epoxides were found by gas chromatography in these reaction mixtures.

Description of the Structure of Cu(HB(3,5-Me$_2$pz)$_3$)(C$_2$H$_4$). The overall structure of Cu(HB(3,5-Me$_2$pz)$_3$)(C$_2$H$_4$) is apparent in the stereoscopic drawing of the molecule (Figure 1) and consists of well-separated neutral monomeric molecules. The copper ion is coordinated to an ethylene molecule and to a nitrogen atom from each of the three 3,5-dimethylpyrazole rings. The complex is essentially trigonally symmetric around the Cu–B axis. This geometry is similar to other four-coordinate complexes with this ligand.[14] Figure 2 shows a view along this axis, in which the displacement of the ethylene molecule off the pseudo-three fold axis toward ring 3 can be seen. The pocket around the the cuprous ion provided by the methyl groups can be seen in Figures 1 and 2.

Selected bond distances and angles are presented in Table X. The observed bond distances and angles for I are nearly identical with those determined in other structures[13,14] and are, therefore, not tabulated here (Table V).[17] Similarly, the Cu-N bond distances and angles are comparable to those previously reported for Cu(I) complexes with I (1.97–2.06 Å, 89–94°).[13,14] The Cu-N contacts are also in the range generally found for Cu(I) complexes with nitrogenous ligands.[13,14,22–24] The Cu–C contacts are typical of Cu(I)–olefin complexes[9a,b,h–k] and of ethylene complexes in general.[9c,25–27] The C–C bond distance of the coordinated ethylene molecule is virtually unchanged from that of the free molecule (1.3371 (2) Å),[25–27] similar to that observed in the crystal structure of IV (vide infra) and shorter than that typically observed for coordinated ethylene molecules.[25–27] There are no other crystallographically characterized Cu(I)–ethylene complexes with which to compare this bond length.[9] However, in the crystal structure of a Cu(I)–1-hexene complex with the ligand diethylenetriamine, the carbon–carbon bond distance of the coor-

Table X. Selected Bond Distances (Å) and Angles (deg) for Cu(HB(3,5-Me$_2$pz)$_3$)(C$_2$H$_4$)

Cu–N11	2.017 (3)	C1–C2	1.329 (9)
Cu–N21	2.041 (3)	B–N12	1.550 (6)
Cu–N31	2.160 (4)	B–N22	1.556 (6)
Cu–C1	2.023 (5)	B–N32	1.549 (6)
Cu–C2	2.004 (6)	B–H(B)	1.068 (41)
N11–Cu–N21	92.4 (1)	N31–Cu–C2	116.7 (3)
N11–Cu–N31	89.8 (1)	N12–B–N22	109.5 (3)
N21–Cu–N31	89.7 (1)	N12–B–N32	109.1 (3)
N11–Cu–C1	148.1 (2)	N22–B–N32	109.1 (3)
N11–Cu–C2	111.1 (2)	N12–B–H(B)	110 (2)
N21–Cu–C1	110.5 (2)	N22–B–H(B)	110 (2)
N21–Cu–C2	143.6 (3)	N32–B–H(B)	108 (2)
N31–Cu–C1	111.5 (2)		

Table XI. Selected Bond Distances (Å) and Angles (deg) for Cu(HBpz$_3$)(C$_2$H$_4$)·CuCl

Cu1–N11	1.934 (2)	N11–Cu1–N21	99.12 (9)
Cu1–N21	1.941 (2)	N11–Cu1–C(1)	111.1 (1)
Cu1–C(1)	2.003 (3)	N11–Cu1–C(2)	150.2 (1)
Cu1–C(2)	1.995 (3)	N21–Cu1–C(1)	149.5 (1)
C(1)–C(2)	1.347 (5)	N21–Cu1–C(2)	110.2 (1)
Cu2–Cl	2.138 (1)	N31–Cu2–Cl	162.77 (7)
Cu2–Cl′	2.714 (1)	Cl–Cu2–Cl′	99.53 (3)
Cu2–N31	1.891 (2)	N31–Cu2–Cl′	97.6 (7)
Cu2–Cu2′	3.165 (1)	N12–B–N22	112.7 (2)
B–N12	1.543 (4)	N12–B–N32	109.6 (2)
B–N22	1.533 (4)	N22–B–N32	108.7 (2)
B–N32	1.550 (4)	N12–B–H(B)	112 (1)
B–H(B)	1.055 (24)	N22–B–H(B)	107 (1)
		N37–B–H(B)	107 (1)

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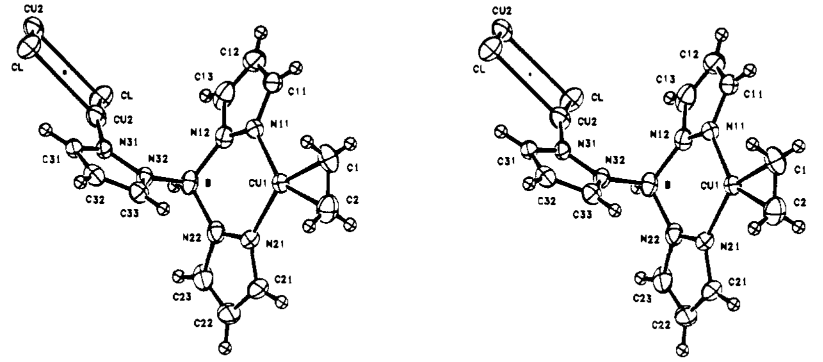

Figure 3. Stereoview of $\mathrm{Cu(HBpz_3)(C_2H_4)\cdot CuCl}$ (IV). The dot represents a center of inversion. The CuCl group from a neighboring molecule is also shown.

dinated olefin was observed to be essentially unchanged from that in the free molecule.[9h] A similar result was also obtained with the chelating olefin 1-allyl-3,5-dimethylpyrazole; a C═C bond distance of 1.34 (2) Å was obtained for the coordinated olefinic bond.[9i]

Description of the Structure of $\mathrm{Cu(HBpz_3)(C_2H_4)\cdot CuCl}$. The overall structure of the complex is apparent in the stereoscopic drawing of the molecule (Figure 3) and consists of weakly associated $\mathrm{Cu(HBpz_3)(C_2H_4)\cdot CuCl}$ units. One copper ion (Cu1) is bonded to two pyrazole groups of II and to an ethylene molecule in a trigonal-planar arrangement. The atoms Cu1, C(1), C(2), N11, and N21 are essentially planar. The third pyrazole ring of II coordinates to a CuCl group, which in turn is weakly associated with the CuCl group of the neighboring molecule. The two CuCl units are related by a center of symmetry (Figure 3).

Selected bond distances and angles are presented in Table XI. The observed bond distances and angles for the coordinated ligand II are nearly identical with those determined in other structures with this ligand[13,21] and are, therefore, not tabulated here (Table IX).[17] There are no unusual features in the coordination sphere of either of the Cu(I) atoms. The Cu1–N and Cu1–C contacts are consistent with other Cu(I) structures.[9,13,21,22-24] Also, the bond angles are in the range expected for a trigonal-planar geometry. The carbon–carbon bond distance of the coordinated ethylene molecule (1.347 (5) Å) is essentially the same as the free molecule value of 1.337 (2) Å[25-27] and that observed for III (1.329 (5) Å) but is on the short end of the range of values observed for coordinated ethylene in general (1.35–1.46 Å)[25-27] and is significantly shorter than the values typically observed to $\mathrm{d^{10}}$ olefin complexes (1.41–1.46 Å).[25] The Cu–N contact for the second copper ion in this molecule, Cu2, is shorter than those observed in three- and four-coordinated complexes,[13,14,21,22] but falls in the range observed for two-coordinate complexes (1.86–1.94 Å).[23],[24] The Cu2–Cl contact is also typical of Cu(I) complexes.[28] The N31–Cu2–Cl bond angle of 162.77 (7)° is somewhat smaller than that generally observed for a linear Cu(I) complex (171–179°).[24] There is, however, a weakly associated CuCl group from a neighboring molecule, with a Cu2–Cl′ distance of 2.714 (1) Å. Although this distance is too great to consider Cu2 to be three-coordinate, this interaction is typical of two-coordinate Cu(I) complexes with nitrogen ligands, which generally have present a weakly interacting atom at a rather long distance.[24a]

Discussion

The objective of the present study was to investigate the coordination chemistry of Cu(I)–monoolefin complexes (particularly with ethylene) to determine whether or not the properties of these complexes are consistent with the role proposed for copper at the ethylene receptor site of plants. The compounds reported here are intended to establish the structural chemistry, physical properties, and reactivities of Cu(I) complexes with the biologically active olefins, rather than to model or suggest active-site structures for the native systems, as there are to date no analytical, spectroscopic, or structural data available on the ethylene binding site. Our approach has been to assemble copper binding environments that approximate those typically found or suggested for Cu(I) ions in biological systems.[12] The polypyrazolyborate ligands I and II provide imidazole-like groups and at the same time limit the mode of coordination of these groups.[13,14] Recent work with imidazole derivatives and other heterocyclic nitrogenous ligands has indicated that the ability of Cu(I) complexes to bind small molecules such as carbon monoxide may be determined by the number and position of these ligands.[23]

The synthetic procedures outlined in eq 1 and 2 yield stable (to loss of olefin) complexes that have been characterized analytically, spectroscopically, and structurally (for III, IV, and VI).[29] The synthetic procedure takes advantage of the formation of Cu(I)–olefin adducts in the presence of excess olefin.[9] Addition of the ligand yields white crystalline solids, which are indefinitely stable under an inert atmosphere. The analytical,[20] infrared, and NMR data are consistent with the formulation indicated for III–VI, but structures for these complexes could not be deduced unequivocally. In particular, the apparent magnetic equivalence at room temperature of the pyrazole rings in IV–VI and the presence of a CuCl moiety, indicated by elemental analysis, made an unambiguous assignment of structure for the complexes impossible on the basis of these data alone. The crystal structure of IV (Figure 3) and VI[29] showed subsequently that there are two different types of rings. Variable-temperature NMR studies were not attempted with III–VI, partly because a similar study with $\mathrm{Cu_2(HBpz_3)_2}$ to −130 °C failed to detect a slow exchange limit for the interchange of bridging and terminal pyrazole groups.[13]

The compounds III and IV establish the types of structures of Cu(I)–ethylene complexes with ligands that approximate polyimidazole binding sites typically found for copper ions in proteins.[11,13,14] Importantly, the structural results obtained here are comparable to the types of structures typically found for the large number of structurally characterized $\mathrm{d^{10}}$ olefin complexes[25,30] and are in accord with the geometries found for Cu(I) complexes in general and for those with the ligands I and II in particular.[13,14,21] Two structural types were found in this study: a four-coordinate tetrahedral geometry for III (Figure 1 and 2) and a three-coor-

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dinate trigonal-planar geometry for IV (Figure 3). Structures similar to IV are proposed or found for V and VI.[29] Numerous structural studies have shown that four-coordinate d^{10} olefin complexes generally have a tetrahedral geometry, whereas three-coordinate complexes are invariably trigonal planar, with the coordinated olefin in the plane defined by the metal atom and the two metal-bound atoms of the other ligands.[25,30] The geometries observed for III and IV are thus not unusual for d^{10} olefin complexes. A surprising result to us initially was the different mode of coordination of ligands I and II. Four-coordinate tetrahedral geometries, the most common for Cu(I) complexes,[14] were anticipated for III–VI, on the basis of the structures of the analogous carbon monoxide complexes (CuL(CO), L = I, II).[13,21] The trigonal-planar geometry was not anticipated for IV. A similar mode of coordination of II has been observed in the complex $Cu_2(HBpz_3)_2$, in which two pyrazole groups of a single $HBpz_3$ moiety are coordinated to different metals, whereas the third ring bridges the two cuprous ions at a distance of 2.660 (1) Å.[13] The results presented here suggest that the trigonal-planar geometry, which is well established for Cu(I) complexes,[9k,23,24] is the dominant structural type for Cu(I)-monoolefin complexes, but tetrahedral complexes can be obtained with ligands that constrain the metal ion to nonplanar interactions. The determination of geometry of monoolefin complexes by choice of ligand has been observed with Ni(0) complexes.[25,31] The majority of these complexes have trigonal-planar geometries, but a tetrahedral Ni(0)–tetrafluoroethylene complex is obtained with the bulky tridentate ligand 1,1,1-tris[(diphenylphosphino)methyl]ethane, which can constrain the metal ion to nonplanar interactions. An important point in regard to the formation of trigonal-planar complexes with II is the requirement for a group such as a CuCl moiety to bind to the third pyrazole ring of II to form the trigonal planar olefin complexes IV–VI. When $[Cu(CH_3CN)_4]ClO_4$[32] was used as a starting material in place of CuCl, the dimer $Cu_2(HBpz_3)_2$ was the only isolated product. With the tetrafluoroborate or hexafluorophosphate analogues of this perchlorate salt,[32] Cu(I)–olefin complexes with a coordinated CuF unit appeared to be the product, on the basis of elemental analysis and infrared and NMR data;[33] we have been unable to confirm this assignment with a crystal structure. Hence, the trigonal-planar geometry does not appear to be the result of the inability of the third ring of II to coordinate to the copper ion but is readily attained when a suitable group is available for coordination to this ring.

An unusual feature of these Cu(I)–ethylene complexes is the relatively short carbon–carbon bond distance of the coordinated olefins: 1.329 (9) Å for III and 1.347 (5) Å for IV. These values are similar to the value reported for the free olefin (1.337 (5) Å).[25-27] Although these short bond distances for coordinated ethylene are not unique (values of 1.319–1.375 Å have been reported),[34] significant lengthening of this bond is generally observed on olefin coordination to d^{10} metal ions (1.41–1.46 Å).[25,26] This similarity in carbon–carbon bond distance between free and coordinated olefin suggests that σ-bonding is the dominant interaction between metal ion and olefin; π-back-bonding from metal to olefin is thus not of great importance. A similar interpretation has been presented to describe the bonding in Ag(I)–olefin complexes.[9c] Structural characterization of other Cu(I)–ethylene complexes is in progress in these laboratories to determine if the relatively unperturbed carbon–carbon distance of the coordinated olefin is a general feature of Cu(I)–ethylene complexes. Relatively short olefinic bond distances have been observed in other structurally characterized Cu(I) complexes,[9] but there are no other structurally characterized Cu(I)–ethylene complexes to compare with III and IV.

Biological Implications. This work demonstrates for the first time that the coordination chemistry of Cu(I)–monoolefin complexes is consistent with the proposed role of copper at the ethylene receptor site of plants. These compounds establish that Cu(I) complexes with imidazole-like ligands do form stable (to loss of olefin) adducts with the biologically active olefins. Further, the geometries observed for the low molecular weight compounds are plausible for Cu(I)–olefin adducts at the active site of proteins, in which tetrahedral and lower coordinate geometries have been established or proposed.[12] The structural results from this study suggest that σ-bonding between the cuprous ion and the coordinated olefin is the dominant interaction. This type of bonding interaction would account at least in part for the observed decrease in biological activity relative to ethylene for olefins with electron-withdrawing groups,[1,5] which would enhance the π-back-bonding from metal to olefin but weaken the σ-donation to the metal ion. The results from this study also show that steric interactions with other metal ligands can be important in determining the olefin coordination in tetrahedral complexes; this type of interaction may explain in part the decrease in biological activity relative to ethylene with increasing molecular size of the olefin; activity decreases along the series ethylene, propylene, 1-butene, 2-butene.[1,5] Although the nature of the ethylene receptor site remains unknown, the properties of the Cu(I) complexes with the biologically active olefins reported here support the suggestion of a copper ion as an ethylene binding site in plant tissue.[4i]

Acknowledgment. The technical assistance of R. M. Swiatek and L. Lardear is gratefully acknowledged. Helpful discussions with Drs. S. D. Ittel, D. L. Thorn, and T. H. Tulip are greatly appreciated.

Registry No. III, 85337-25-3; IV, 85337-26-4; V, 85337-27-5; VI, 85337-28-6; $HB(3,5\text{-}Me_2pz)_3\cdot K$, 17567-17-8; $HBpz_3\cdot K$, 18583-60-3; ethylene, 74-85-1; cuprous iodide, 7681-65-4; cuprous chloride, 7758-89-6; cyclohexene, 110-82-7.

Supplementary Material Available: Tables of final positional and thermal parameters (Tables II and VI), general temperature factors (Tables III and VII), structure amplitudes (Tables IV and VIII), and bond distances and angles (Table V and IX) (51 pages). Ordering information is given on any current masthead page.

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