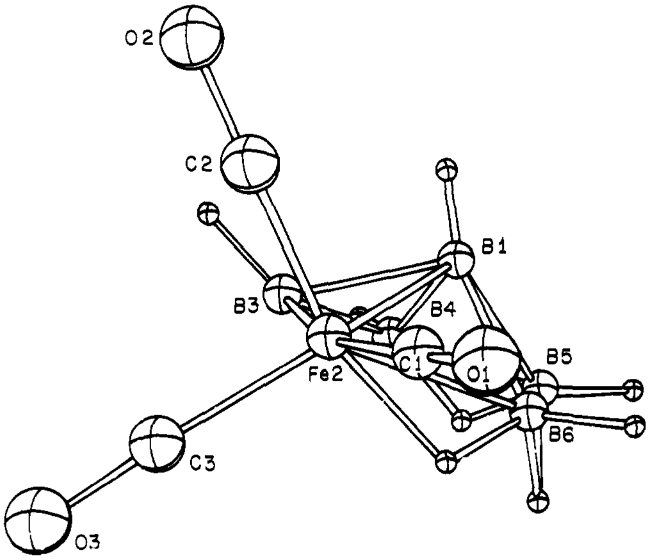

Figure 2. Structure of $Fe(CO)_3B_5H_8^-$.

of hydrogen between Fe and B6 suggests that it is a bridging hydrogen.

In view of the similar NMR spectra of $B_5H_9Fe(CO)_3$ and $B_5H_8Fe(CO)_3^-$, we assume that they are structurally similar and that the unique H on Fe has the same characteristics in the neutral and anionic species. The apparent spin coupling of this hydrogen with boron-11 atoms adjacent to Fe (determined by narrow line spin decoupling) is consistent with, though not necessarily confirming, the existence of an Fe-H-B bridge. If such is the case, then $B_5H_9Fe(CO)_3$ and $B_5H_8Fe(CO)_3^-$ can be represented by valence structures analogous to B_6H_{10} and $B_6H_9^-$, respectively, with $Fe(CO)_3$ replacing a vertex and serving as a formal two-electron donor to the polyhedral skelton.[11] However, valence level photoelectron spectra are consistent with an electronic structure in which this hydrogen behaves as a terminal Fe-H.[12] Since the hydrogens were not refined in the x-ray crystal structure determination, caution must be exercised in drawing conclusions from the apparent Fe-H distance (1.52 Å). Interestingly, however, this distance is close to the values observed (1.51 (9)-1.57 (12) Å)[13] for terminal Fe-H bonds and is appreciably shorter than is observed in Fe-H-Fe bridging systems (1.79 (13)-1.82 (13) Å).[14] The apparent B6-H distance of 1.15 Å is slightly larger than the usually observed value for a terminal B-H bond.[15] We look to further chemical and spectroscopic experiments for elucidation of the nature of this unique hydrogen.

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Oxidative Decarboxylation of a Tripeptide. The Reaction of Copper(II) Hydroxide and Glycylglycyl-L-histidine

Sir:

Recent work by Sarkar and co-workers[1] has demonstrated that the peptide molecule glycylglycyl-L-histidine (glygly-L-his) is a good model for the specific copper(II) transport site of human serum albumin, and this has led to extensive research on the complexes formed by copper(II) with glygly-L-his;[1-4] there had already been a number of investigations of copper(II) complexes of gly-L-his-gly.[5-7] Sarkar and co-workers[1-4] have suggested that the copper(II) complex of glygly-L-his has a square planar structure in which the metal is coordinated to four nitrogen atoms of the tripeptide; a recent crystallographic study of a complex of a derivative of the tripeptide[8] has tended to confirm this view. In attempting to isolate crystals of the parent complex, [Cu(glygly-L-his)], we chose to use the hydroxide as our source of the metal since this starting material was used[9,10] to obtain crystals of copper peptide complexes and has been found to be successful in our laboratory in the preparations of $Cu(L\text{-met})_2$ and $Zn(L\text{-met})_2$.[11] Upon examining the product of this reaction by single-crystal x-ray diffraction methods we discovered that the tripeptide had undergone an oxidative decarboxylation but that the final product had the anticipated square planar coordination around the copper(II) center.

The complex was prepared by mixing freshly prepared copper(II) hydroxide (1×10^{-3} mol) and glygly-L-his (1×10^{-3} mol) in water (15 ml) at room temperature. The copper(II) hydroxide was prepared from copper(II) chloride and sodium hydroxide in the normal manner.[10] The crystals are triclinic, space group $P\bar{1}$, with two molecules in a cell of dimensions $a = 7.315$ (2) Å, $b = 10.110$ (3) Å, $c = 9.609$ (3) Å, $\alpha = 71.59$ (3)°, $\beta = 86.66$ (2)°, and $\gamma = 110.74$ (2)°. The calculated density of 1.721 g cm^{-3} is in acceptable agreement with the observed value of 1.69 g cm^{-3}. Crystallographic intensity data were collected on a Picker four-circle automatic diffractometer to $2\theta = 60°$, using Mo Kα radiation and a graphite monochromator. The structure was solved by stan-

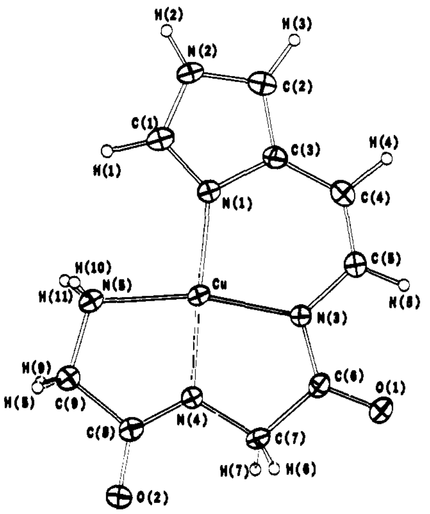

Figure 1. View of the complex of the oxidative decarboxylation product of glygly-L-his and copper(II). Hydrogen atoms are shown as spheres of arbitrary size; other thermal ellipsoids are at the 40% probability level.

dard heavy atom methods; full-matrix least-squares refinement (including all of the hydrogen atoms as fixed contributors) has now reached a conventional R factor of 0.038 based on 1636 independent intensities.

The structure contains the four-coordinate complex shown in Figure 1 and two water molecules. The central copper atom has approximate square planar geometry, with the four ligand nitrogen atoms bonded at normal distances[8] of 1.898 (3) to 2.028 (4) Å. The decarboxylation has occurred at atom C(5), with deprotonation at C(4) to give a formal double bond between these two atoms. The C(4)–C(5) bond length of 1.340 (6) Å is consistent with this model, and is much shorter than the values of 1.525 (6) and 1.536 (5) in [Co(L-his)(D-pen)]·H_2O and [Cu(gly-L-his-gly)]·$2\frac{1}{2}H_2O$, respectively;[12,13] in L-histidine, the value is 1.536 (3) Å.[14] As expected, the adjacent bonds C(3)–C(4) and C(5)–N(3) are slightly shorter than in L-histidine and these other complexes;[12-14] all other distances in the ligand are normal.

The two water molecules form hydrogen bonds to the ligand oxygen atoms O(1) and O(2), but are not involved in the copper coordination sphere. Atom O(1) forms a hydrogen bond to both water molecules, while atom O(2) forms a hydrogen bond to one water molecule and an intermolecular hydrogen bond to the imidazole nitrogen atom N(2) of an adjacent ligand.

In view of the unexpected oxidative decarboxylation, the integrity of the starting tripeptide sample was checked by amino acid analysis and found to have the correct 2:1 ratio of gly to his; thus, there is no doubt that the starting material was the tripeptide. It is noteworthy that the copper complex is very stable, and can be recrystallized from boiling water.

Oxidative decarboxylations of organic acids by metal salts (notably by lead tetraacetate in the presence of copper(II) acetate) have been described before,[15-19] but in these previous examples the product of the reaction was the stable, free olefin. The present example is the first, to our knowledge, of an oxidative decarboxylation of a peptide, and also the first in which the resulting product is tightly coordinated to the metal. The mechanism of this reaction is currently under investigation.

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Photochemistry in the Electronic Ground State. 4. Infrared Laser Induced Isomerization of Labeled Compounds. A Possible Route for Isotope Separation

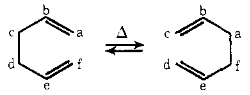
Sir:

We wish to report a quantitative isotope-selective isomerization induced by a CO_2 laser.

In previously published work performed in our laboratory, we were able to interrupt the chemical equilibrium of the cis-trans isomerization of 2-butene.[1] The partial isomerization of this reaction was accompanied by selective decomposition of the absorbing component of the reaction mixture.

Many other reports on selective reactions induced by infrared lasers dealt merely with decomposition of the absorbing species.[2]

In the present study we have investigated the reversible Cope rearrangement of 1,5-hexadiene (biallyl) labeled with deuterium at specific positions. In this system the starting material and product are chemically identical and differ only in the position of the deuterium labeling. The reaction is defined as a [3*S*,3*S*]sigmatropic shift,[3] therefore allowed via electronic ground state. The energy of activation is 34.3 kcal mol^{-1},[4] and the secondary isotope effect is 10% per atom at room temperature in favor of deuterium at allylic positions.[5]



The experimental set-up employed in the present experiments consisted of a pulsed CO_2 TEA laser,[1] equipped with a diffraction grating. Pulse duration of about 100 ns and peak power of 0.3 MW at optimal conditions were measured by a photon-drag detector. The beam was focused by a 20 mm focal length mirror into the irradiation cell, previously described.[1]

Irradiation of biallyl was performed at pressures ranging from 5 to 16 Torr. At higher pressures a breakdown, leading