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(10) Separated by preparative TLC (silica gel); isomer A[7] (oil, ν_{max}^{neat} 3370, 3230, 1634, 910 cm^{-1}, δ^{CDCl_3} 8.3 (1 H, br s), 6.05–5.55 (1 H, m), 5.5–4.95 (4 H, m)) and isomer B[7] (oil, ν_{max}^{neat} 3360, 3230, 1634, 910 cm^{-1}, δ^{CDCl_3} 8.1 (1 H, br s), 6.05–5.50 (1 H, m), 5.5–4.8 (4 H, m)).

(11) Preparative TLC (silica gel) separation furnished α-ethyl isomer (mp 157–158 °C; ν_{max}^{Nujol} 3300, 1638, 908 cm^{-1}; δ^{CDCl_3} 7.9 (1 H), 6.03–5.6 (1 H, m), 5.5–4.98 (3 H, m), 0.72 (3 H, t, J = 7 Hz)) and β-ethyl isomer (oil, ν_{max}^{neat} 3250, 1636, 910 cm^{-1}; δ^{CDCl_3} 8.1 (1 H), 5.83–4.8 (3 H, m), 0.97 (3 H, t, J = 7 Hz)).

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The Ferraborane $B_5H_9Fe(CO)_3$ and Its Conjugate Base $B_5H_8Fe(CO)_3^-$

Sir:

We have isolated an unstable ferraborane, $B_5H_9Fe(CO)_3$, which appears to be the precursor of $B_4H_8Fe(CO)_3$.[1] The reaction of B_5H_9 with $Fe(CO)_5$ in a hot-cold reactor maintained at 220 °C/20 °C for ca. 3 days with frequent removal of evolved CO yielded $B_5H_9Fe(CO)_3$, which was separated from other products by low-temperature fractionation. This compound is a red liquid and is sensitive to both light and heat. Its mass spectrum exhibited a high mass cutoff at m/e = 204 with fragment ions corresponding to the successive loss of three CO molecules. Relative intensity distributions of the parent ion cluster and those fragments due to loss of CO were characteristic of a compound containing five boron atoms (obsd 87:100:59:21; calcd 80:100:49:12).[2] Precise mass measurements on the m/e 204 ion yielded a composition of $^{11}B_5{}^1H_9{}^{12}C_3{}^{16}O_3{}^{56}Fe$ (obsd 204.036 ± 0.002 amu; calcd 204.037 amu).

Structural information from ^{11}B and ^1H NMR spectra are consistent with a pyramidal structure which contains an $Fe(CO)_3$ group at a basal vertex (Figure 1). For reasons given below, the hydrogen which is bound to Fe is not clearly a bridging hydrogen. Boron-11 NMR spectra in CH_2Cl_2 at ambient temperature are indicative of C_s symmetry, showing two basal doublets of intensity ratio 2:2 at −46.1 ppm (J, 150 Hz) and −8.6 ppm (J, 150 Hz), compared to an apical resonance of intensity 1 at 47.2 ppm (J, 140 Hz) relative to BF_3OEt_2 at 0 ppm. Severe broadening of these resonances occurred at lower temperatures. The most striking feature of ^1H NMR spectra is the presence of a temperature invarient resonance over the range studied (30 to −100 °C), which appeared as a single broad peak at τ 26.82 (Me_4Si τ 10.00). This resonance can only be due to a proton which is bound to Fe.[3] Boron-11 spin-decoupling causes this resonance to sharpen. While these results suggest a possible static Fe–H–B bridging system[4] on the NMR time scale, the proton NMR spectra of the remaining basal protons and ^{13}C NMR are clearly consistent with a fluxional system. At −35 °C a single averaged resonance for protons bridging boron atoms (τ 9.90) and two averaged resonances representing the two sets of terminal basal protons are observed (τ 3.60, 5.81). Below −70 °C the bridge resonance splits into three peaks of equal intensity (τ 9.18, 9.92, 10.72) and each basal terminal resonance splits into two resonances of equal intensity (τ 3.16, 4.03, 5.48, 6.14). The apical resonance is temperature independent (τ 11.19). The ^{13}C NMR spectrum reveals a single resonance at −30 °C (207.9 ppm downfield of Me_4Si) which splits into three resonances of equal intensity below −120 °C (210.5, 207.7, 206.6 ppm).

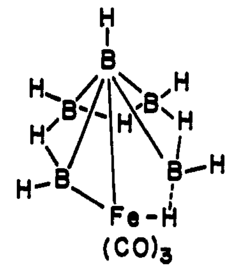

Figure 1. Proposed structure of $Fe(CO)_3B_5H_9$.

The fluxionality is believed to arise from movement of the H on iron between the two possible bridging sites either through rotation or pseudorotation of the $Fe(CO)_3H$ group. If the H on Fe is involved in three-center bonding with boron, the breaking of this bond occurs as Fe–HB rather than the commonly observed M H–B in other fluxional metalloboranes.[5] Thus hydrogen on iron might be termed a "pseudo" terminal hydrogen, since it appears always to be associated with Fe throughout the fluxional process.

The following deprotonation reaction was observed.[6]

$$B_5H_9Fe(CO)_3 + KH \xrightarrow[-78\ °C]{(CH_3)_2O} K^+\ B_5H_8Fe(CO)_3^- + H_2$$

Boron-11 and proton NMR spectra of $KB_5H_8Fe(CO)_3$ in $(CD_3)_2O$ are very similar to the spectra of $B_5H_9Fe(CO)_3$ with respect to appearance and temperature dependence except that the low temperature (−140 °C) ^1H NMR spectrum of $B_5H_8Fe(CO)_3^-$ reveals only two bridge resonances (1:1 relative areas), rather than the three bridge resonances observed in the ^1H NMR spectrum of $B_5H_9Fe(CO)_3$. This indicates that a B–H–B bridging proton has been removed in the deprotonation process. Furthermore, a temperature-independent resonance at τ 26.0 indicates that an H associated with Fe exists in the anion as well as in the neutral molecule. Boron-11 spin decoupling causes this resonance to sharpen.

From the following metathesis reaction, crystals of $N(n\text{-}C_4H_9)_4^+B_5H_8Fe(CO)_3^-$ were obtained.

$$K^+\ B_5H_8Fe(CO)_3^- + N(n\text{-}C_4H_9)_4^+\ Br^- \xrightarrow[-23\ °C]{CH_2Cl_2} N(n\text{-}C_4H_9)_4^+\ B_5H_8Fe(CO)_3^- + KBr$$

The crystals are monoclinic (space group $P2_1/b$): a = 11.108 (6), b = 15.462 (12), c = 15.443 (9) Å, γ = 95.87 (5)°. Assuming Z = 4, d calcd = 1.10 g/cm^3. Of the 3893 independent reflections measured 1557 had $I \geq 3\sigma(I)$ and were considered observed. Patterson and Fourier[8] techniques gave the positions of the nonhydrogen atoms. Methylene hydrogen atoms of the cation were placed at their calculated positions and the weighting scheme of Clayton, Mangion, and Meyers[8] was employed to obtain a weighted difference electron density synthesis from which approximate coordinates of hydrogens on the anion were obtained. Due to the limited number of observed reflections the hydrogens were not refined and anisotropic refinement of heavier atoms was not attempted. Full matrix least-squares refinement converged with a conventional R of 0.080 and a weighted R of 0.092.[7]

The structure of $B_5H_8Fe(CO)_3^-$ is given in Figure 2. This structure is like the proposed structure of $B_5H_9Fe(CO)_3$ except that the bridging H between B3 and B4 is absent. The three Fe–B distances are B1–Fe = 2.16 (1), B3–Fe = 2.08 (2), and B6–Fe = 2.13 (2) Å. These distances appear shorter than the B–Fe distances of 2.22 (1) and 2.20 (1) Å for iron in a bridging position in μ-$Fe(CO)_4$-$B_7H_{12}^-$.[9] The angle B3–Fe–B6 = 83.5 (6)° is much wider than is observed for Fe in a bridging position, B–Fe–B = 47.4 (3)°, in μ-$Fe(CO)_4$-$B_7H_{12}^-$.[9] Within the boron framework the distances appear normal.[10] The position

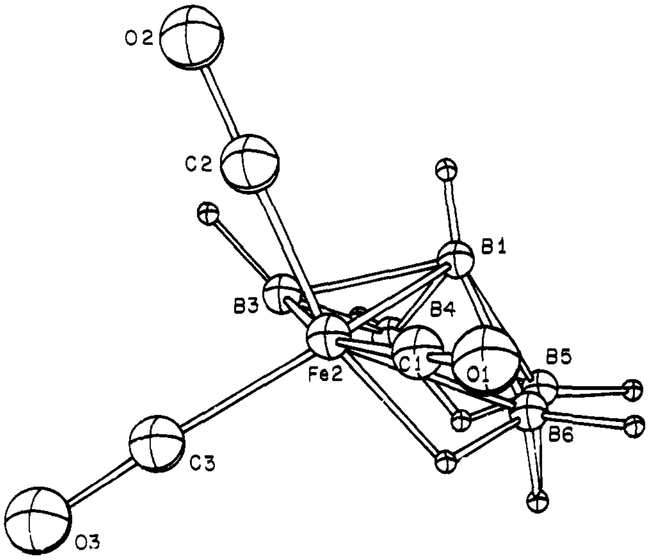

Figure 2. Structure of $Fe(CO)_3B_5H_8^-$.

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 $Cu(\text{L-met})_2$ and $Zn(\text{L-met})_2$.[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 $K\alpha$ radiation and a graphite monochromator. The structure was solved by stan-