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Which Metallaborane, $B_2H_5FeCo(CO)_6$ or $B_2H_6Fe_2(CO)_6$, Has the Higher Brønsted Acidity?

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Summary: The mixed-metal metallaborane $B_2H_5FeCo(CO)_6$ is obtained in good yield from the reaction of $B_2H_6Fe_2(CO)_6$ with $Co_2(CO)_8$. The Brønsted acidity, relative to $B_2H_6Fe_2(CO)_6$, is measured by proton competition between neutrals and anions. Contrary to conventional wisdom, replacement of Fe + H by Co in a strictly isoelectronic system decreases the Brønsted acidity of the cluster. It is proposed that the change in number of framework hydrogens has a greater effect on the cluster acidity than does the heterometal.

The effect of heterometals on the Brønsted acidities of organometallic compounds has been a topic of longstanding interest.[1] Systematic studies have shown that for mononuclear complexes the acidity decreases as one goes down a column of the periodic table and increases from left to right; e.g., $HMn(CO)_5 < H_2Fe(CO)_4 < HCo(CO)_4$.[2] Ancillary ligands have a substantial effect on the acidity,[3,4] but, as long as the ligand type is constant, trends with the metal are established. For clusters, it is known that the acidity of a M–H–M bridging hydrogen is higher than that of a M–H terminal hydrogen due to delocalization of the negative charge on the conjugate base. Interstitial hydrogens exhibit related behavior.[5]

Consistent with the known acidity of B–H–B hydrogens,[6] as well as that of M–H–M hydrogens, the B–H–Fe hydrogens in ferraboranes exhibit protonic character and the conjugate anions resulting from deprotonation permit the development of a derivative chemistry.[7] In order to explore the effects of heterometals, we have now prepared cobalt analogs of $B_2H_6Fe_2(CO)_6$ (Figure 1a),[8] fully expecting an increase in Brønsted acidity. As demonstrated in the following for $B_2H_5CoFe(CO)_6$, this is not the case.

In contrast to related substitution reactions with other anionic clusters,[9] neither $[B_2H_5Fe_2(CO)_6]^-$ nor $[B_2H_4Fe_2(CO)_6]^{2-}$ yields any isolatable products on reaction with $Co_2(CO)_8$. However a mixed-metal analog can be prepared by a fragment exchange reaction of $Co_2(CO)_8$ with $B_2H_6Fe_2(CO)_6$.[10] The proposed structure of $B_2H_5CoFe(CO)_6$ is shown in Figure 1b.[10] Although it has not been crystallographically characterized, this structure is firmly based on the known structures of $B_2H_6Cp^*{}_2Ta_2Br_2$[11] and $[B_2H_4Fe_2(CO)_6]_2$.[12] Only two arrangements of hydrogens are permitted by the spectroscopic data, namely those shown in Figure 1b,c. A partially resolved splitting of the resonance for the M–H–B protons at δ −15.2 at −90 °C (∼0.04 ppm at 300 MHz, FWHM = 44 Hz) is observed. The splitting is attributed to a J_{HH} coupling (H_t–H_b; ∼12 Hz

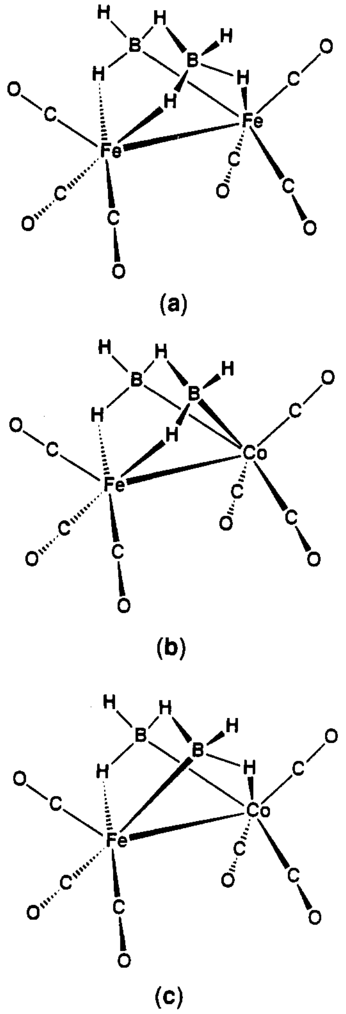

Figure 1. Schematic drawings of the proposed structures for (a) $B_2H_6Fe_2(CO)_6$, (b) $B_2H_5FeCo(CO)_6$ (more stable), and (c) $B_2H_5FeCo(CO)_6$ (less stable).

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[10] The reaction of $B_2H_6Fe_2(CO)_6$ with an excess of $Co_2(CO)_8$ in hexane at 70 °C over a period of 6 h leads to the formation of a number of products. Vacuum-line fractionation (−20 °C) permitted the isolation of an orange air-sensitive oil, $B_2H_5FeCo(CO)_6$, in 34% yield based on the ferraborane. MS/EI: P^+ *m/e* 310 (2B − 6CO), calcd $^{12}C_5{}^1H_5{}^{16}O_5{}^{11}B_2{}^{56}Fe^{59}Co$ 281.9041, obsd 281.9021. IR (hexane, cm^{-1}): 2530 vw, 2098 w, 2054 vs, 2034 s, 2007 m. NMR: ^{11}B (hexane, 22 °C, δ) −13.5 (br d, J_{BH} = 144 Hz) ($^{11}B\{^1H\}$ br s); ^1H (toluene-d_8, 22 °C, δ) 2.24 (br, 2H), −2.68 (br, 1H), −15.17 (br, 2H).

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vs 7.2 Hz in B_2H_6 and 20 Hz in $[HFe_3(CO)_9H_2BH]^-$)[13,14] in Figure 1b rather than fortuitous overlap of FeHB and CoHB resonances. The latter is possible but is considered less likely.

Reaction of $B_2H_6Fe_2(CO)_6$ with NEt_3 leads to $[B_2H_5Fe(CO)_6]^-$, which has the same number of protons as $B_2H_5CoFe(CO)_6$. Mössbauer spectroscopy of $[B_2H_5Fe_2(CO)_6]^-$ in the solid state showed the presence of two tautomers with structures corresponding to those in parts b and c of Figure 1 in the ratio of 3:1.[8] This is consistent with our assignment of Figure 1b to $B_2H_5CoFe(CO)_6$. Reaction of $B_2H_5CoFe(CO)_6$ with NEt_3 in hexane leads to a yellow precipitate which quantitatively regenerates $B_2H_5CoFe(CO)_6$ on protonation with CF_3COOH. Clearly the precipitate is $[B_2H_4CoFe(CO)_6]^-$, but further characterization was not possible due to rapid ($t_{1/2} < 5$ min) decomposition of this material in polar solvents to yield $BH_3{\cdot}NEt_3$ and other products. This accounts for our inability to obtain the mixed-metal compound by fragment exchange with the ferraborane anions.

Considering the trends in acidity established for mononuclear compounds, we expected the Brønsted acidity of the bridging hydrogens to increase with the replacement of Fe + H by Co in the $B_2H_xM_2(CO)_6$ framework. Proton competition reactions were used to demonstrate relative acidities.[15] No reaction of $[B_2H_5Fe_2(CO)_6]^-$ with $B_2H_5FeCo(CO)_6$ is found, but the reaction of $[B_2H_4FeCo(CO)_6]^-$ with $B_2H_6Fe_2(CO)_6$ leads to the formation of $[B_2H_5Fe_2(CO)_6]^-$ and $B_2H_5FeCo(CO)_6$.[16] This shows that the substitution of Co for Fe *decreases* the Brønsted acidity of the bridging hydrogens.

We are forced to conclude that the origin of the higher acidity of $B_2H_6Fe_2(CO)_6$ lies in the differing numbers of framework hydrogens on the isoelectronic clusters. The only difference between $B_2H_6Fe_2(CO)_6$ and $B_2H_5FeCo(CO)_6$ is that an unshielded proton in the former becomes a highly shielded proton in the latter, as it now resides in the metal nucleus. If the effect of the proton is transmitted throughout the cluster network, the acidity of the Fe_2 compound will be enhanced relative to the FeCo compound. This suggestion is consistent with our previous comparison of the organometallic clusters $Co_3(CO)_9CCH_3$ and $HFeCo_2(CO)_9CCH_3$ in that the symmetric CO stretch (highest frequency band) is higher in energy for the latter.[17]

Even in isoelectronic clusters, the ancillary ligands determine certain cluster properties. In this case the effect of the number of hydrogens overwhelms the more subtle effects of changing the identity of the transition metal. Insofar as the cluster–surface analogy is valid,[18] this suggests that the protonic character of a bridging hydrogen atom on a metal surface will be affected by the presence or absence of nearby bridging hydrogens.

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